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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.

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Standoff Detection of Persistent Chemical Agents on Surfaces

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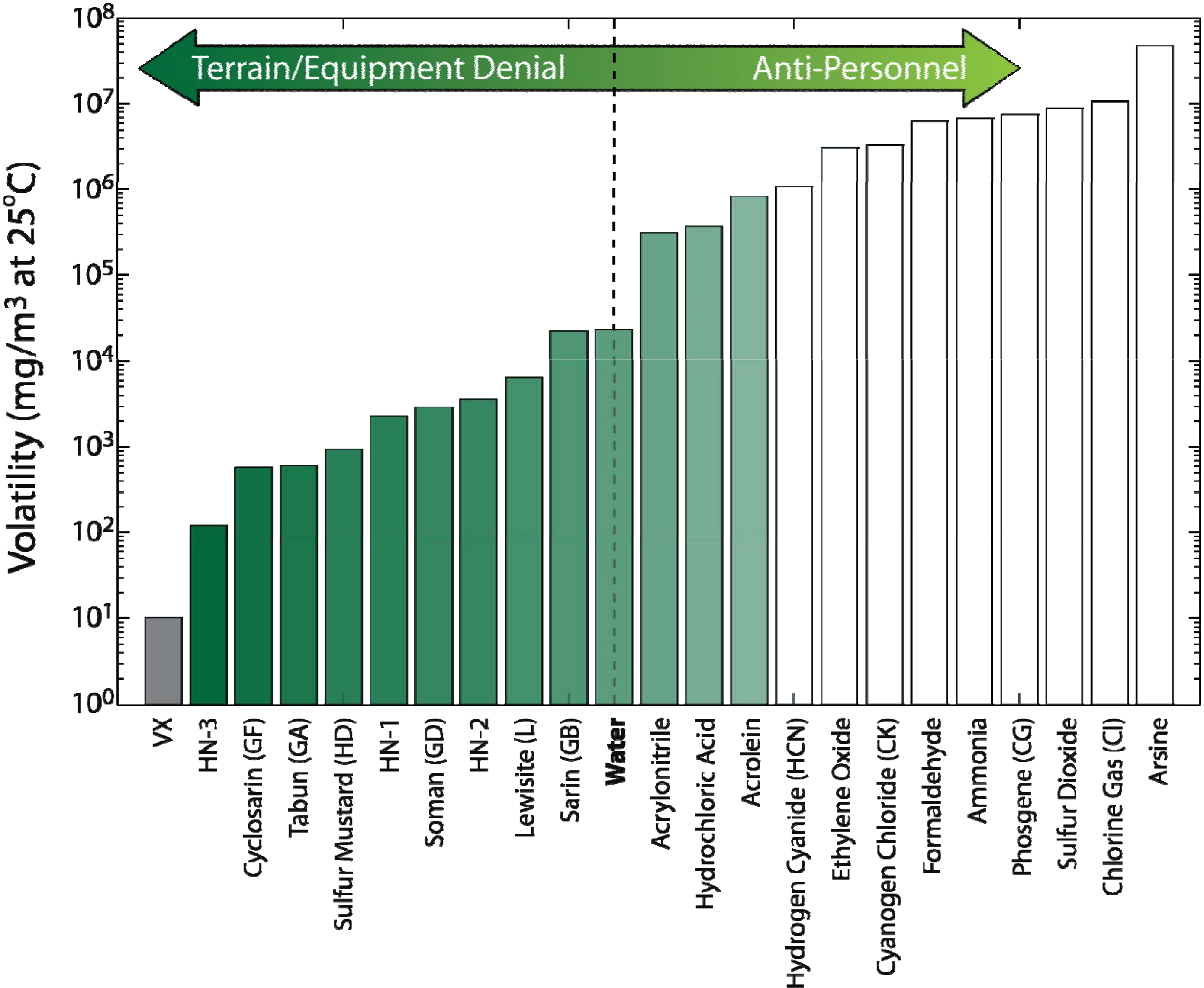
Persistent Chemical Agents on Surfaces

- **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

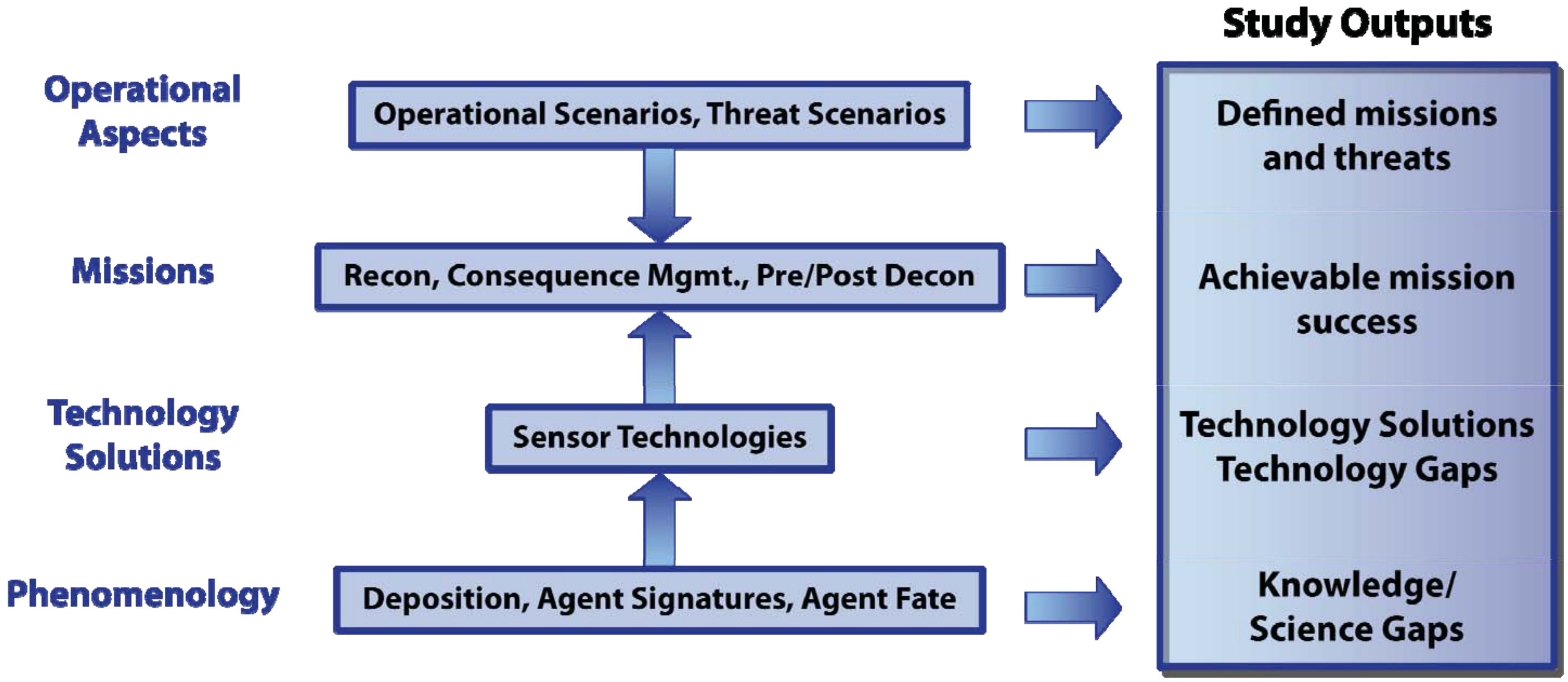


Primary use of agents (**Terrain and Equipment Denial** vs. **Anti-Personnel**) and primary hazard (**Inhalation** vs. **Contact**) vary with persistence

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



Study Outputs

Operational Aspects
Operational Scenarios, Threat Scenarios
Defined missions and threats

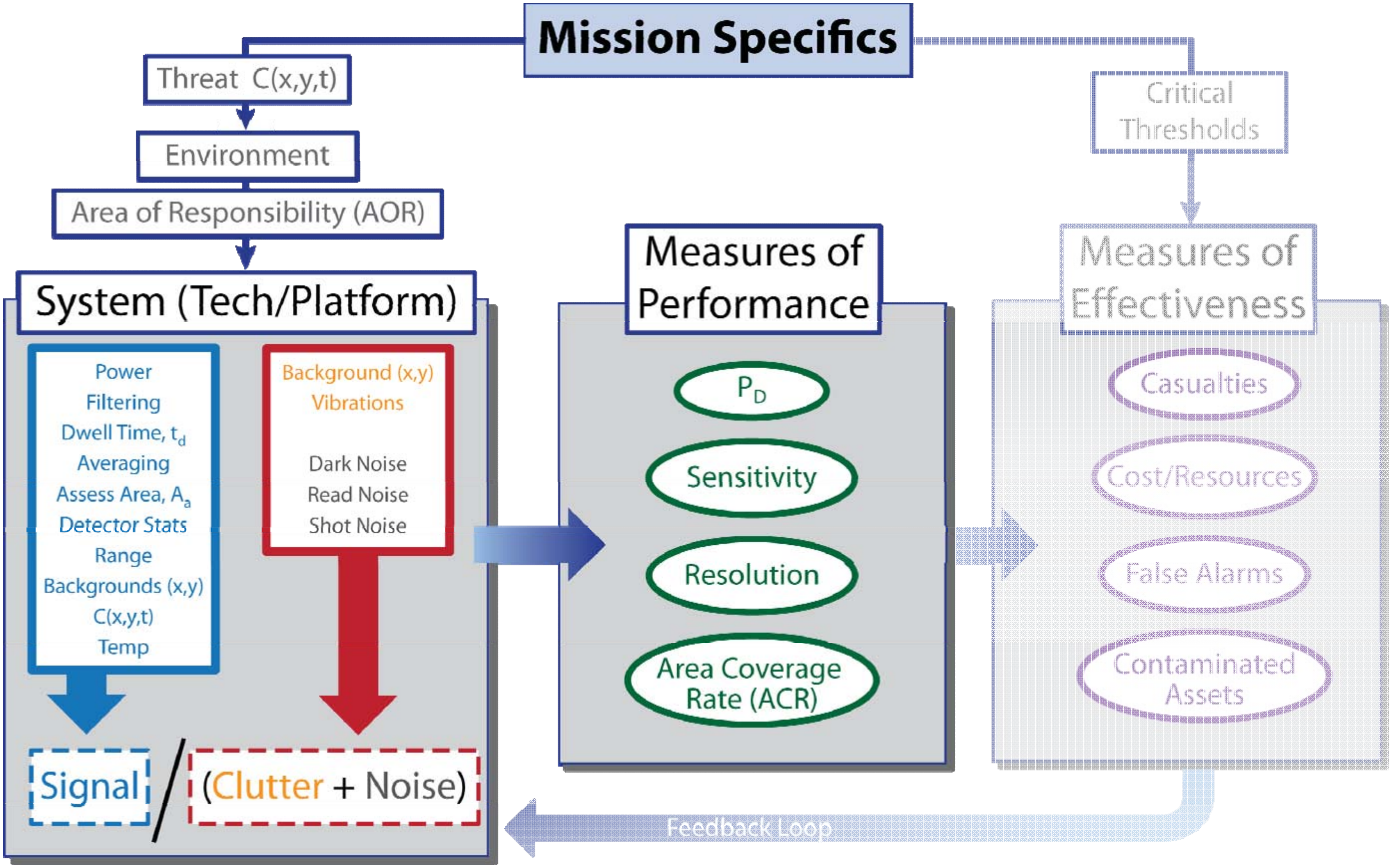
Missions
Recon, Consequence Mgmt., Pre/Post Decon
Achievable mission success

Technology Solutions
Sensor Technologies
Technology Solutions Technology Gaps

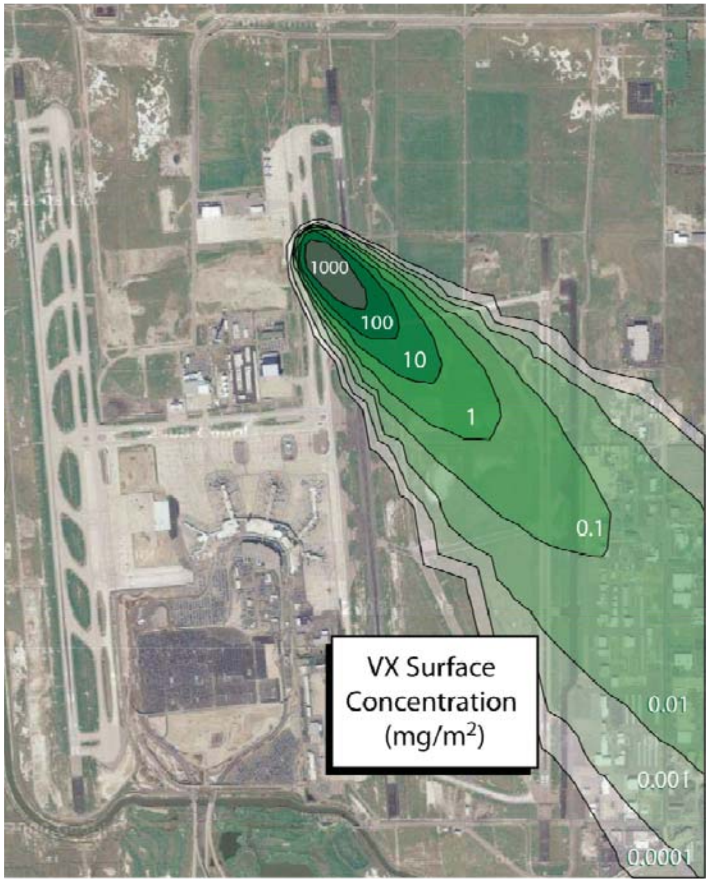
Phenomenology
Deposition, Agent Signatures, Agent Fate
Knowledge/ Science Gaps

Subset of Results on Sensor Technologies Shown Today

System Analysis Process



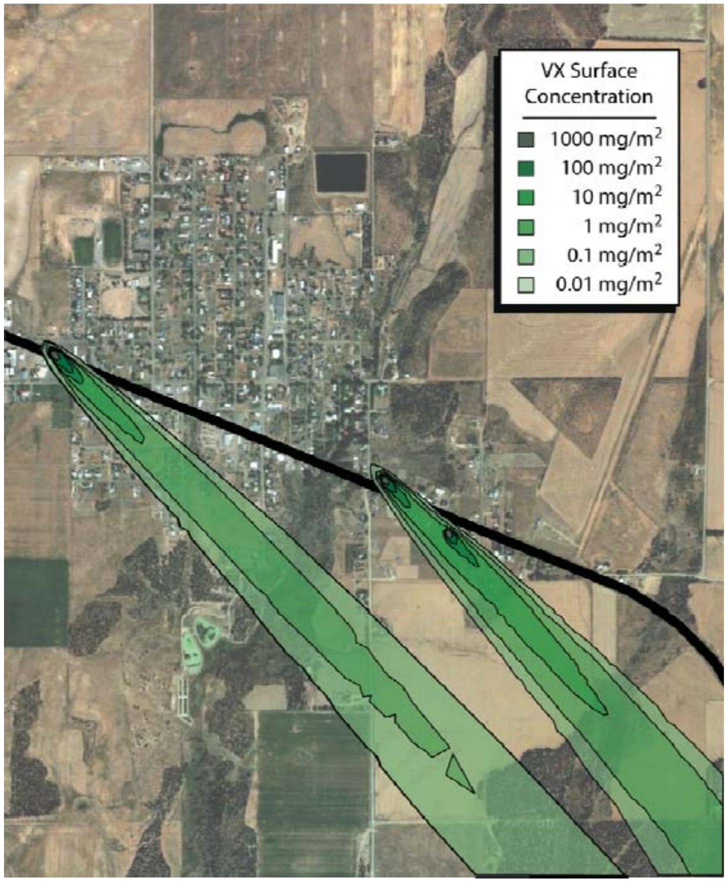
Mission Scenarios



Fixed Site

Thickened VX Scud Detonates

Goal: Mapping for
Consequence Management



Maneuver

VX Sprayers Used Along Route

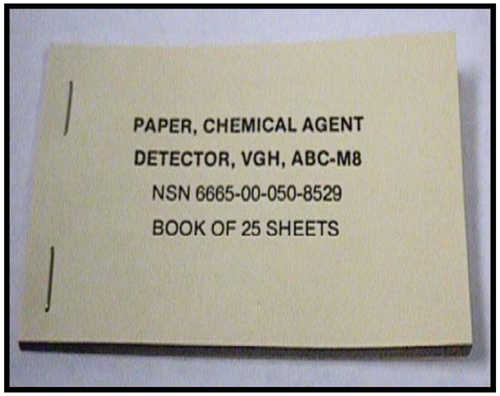
Goal: Warning for
Contamination Avoidance

Operational Use Requirements

- Sensitivity: **0.1 mg/m^2**
  - LD$_{50}$ 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 (0.015m^2)
- 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

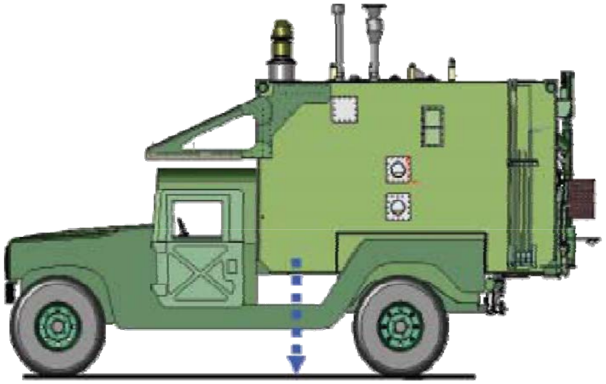


- Standardized in **1963**
- Personnel contamination
- Very slow
- False positives
- Pro: Easy to use

M93 Fox, double wheeled sampler, Mass Spec

- Approved for fielding in **1995**
- Vehicle contamination
- Slow, 2kph
- Narrow spatial coverage

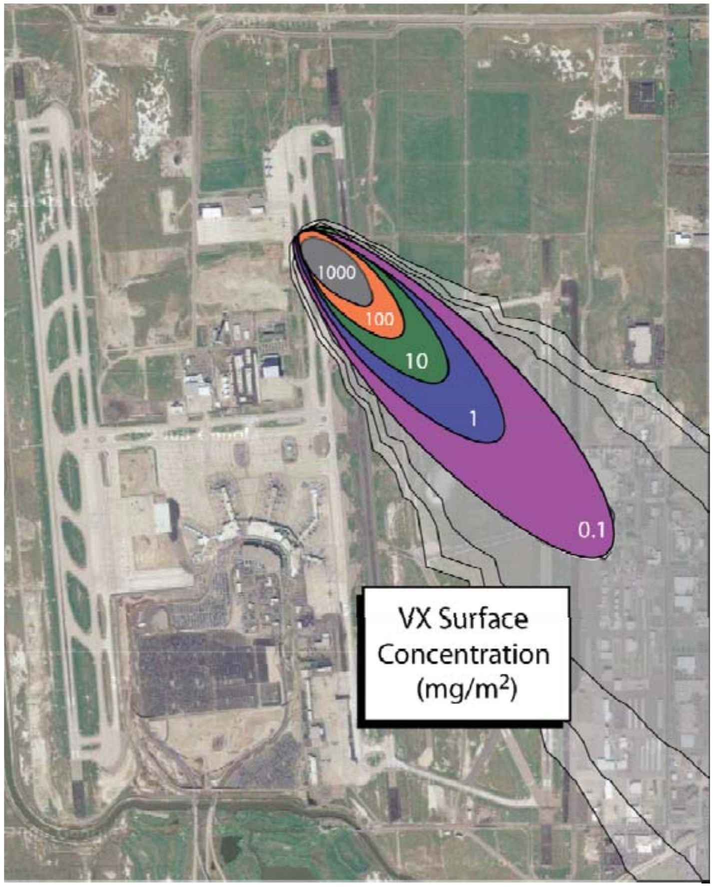
JCSD (Emerging): Raman System



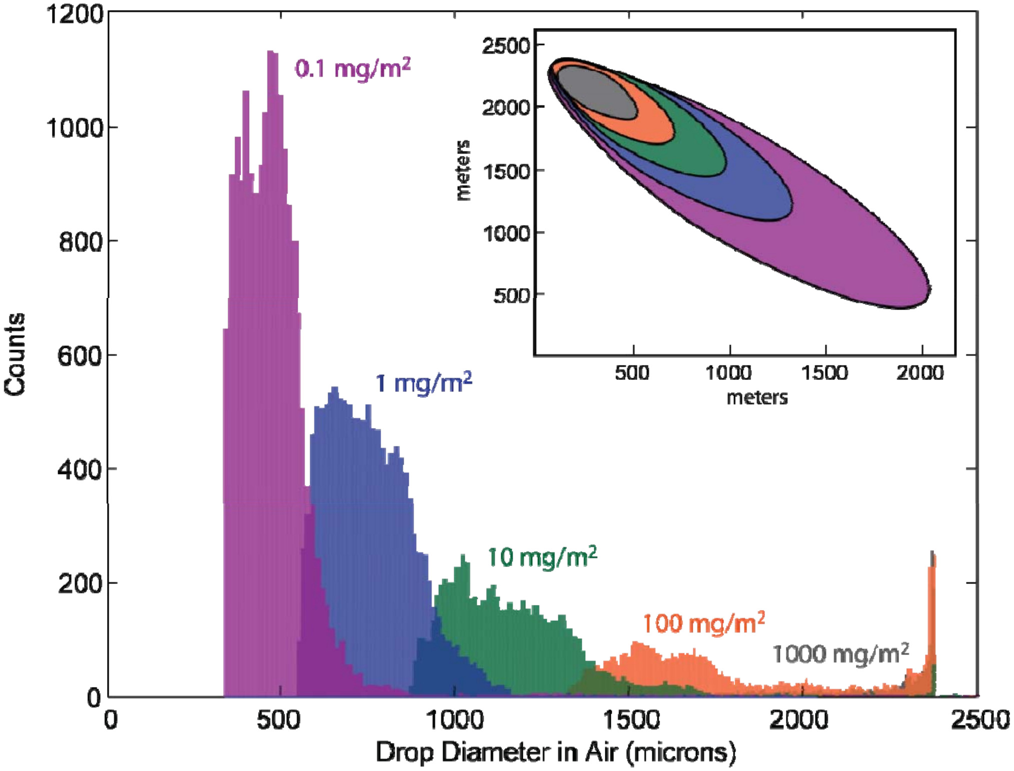
- Developed starting in **2001**
- Vehicle contamination
- Narrow spatial coverage
- Pro: Fast road coverage

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

Fixed Site: Drop Sizes

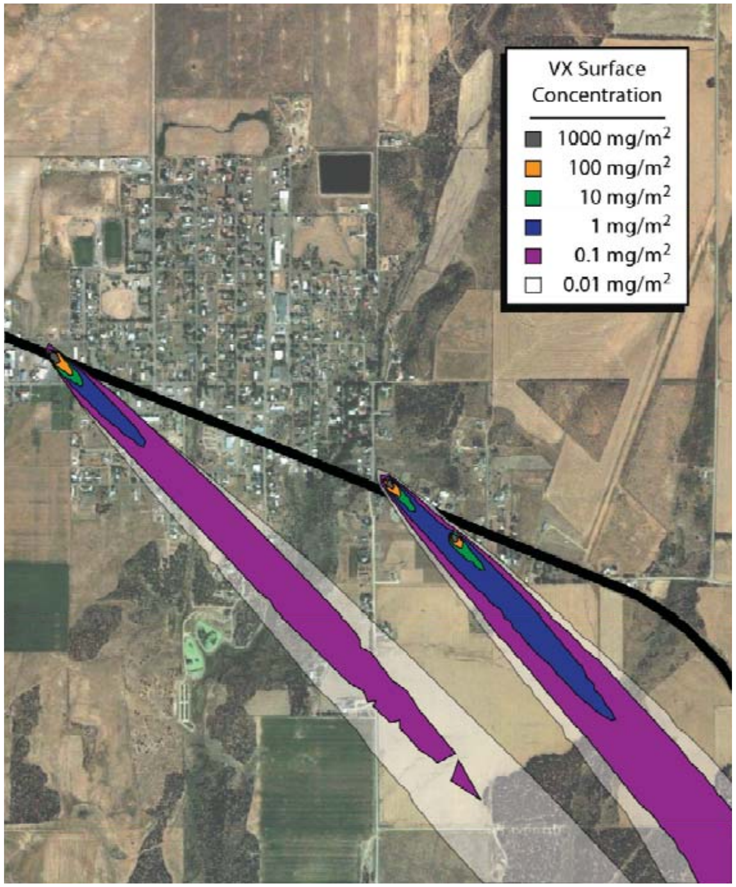


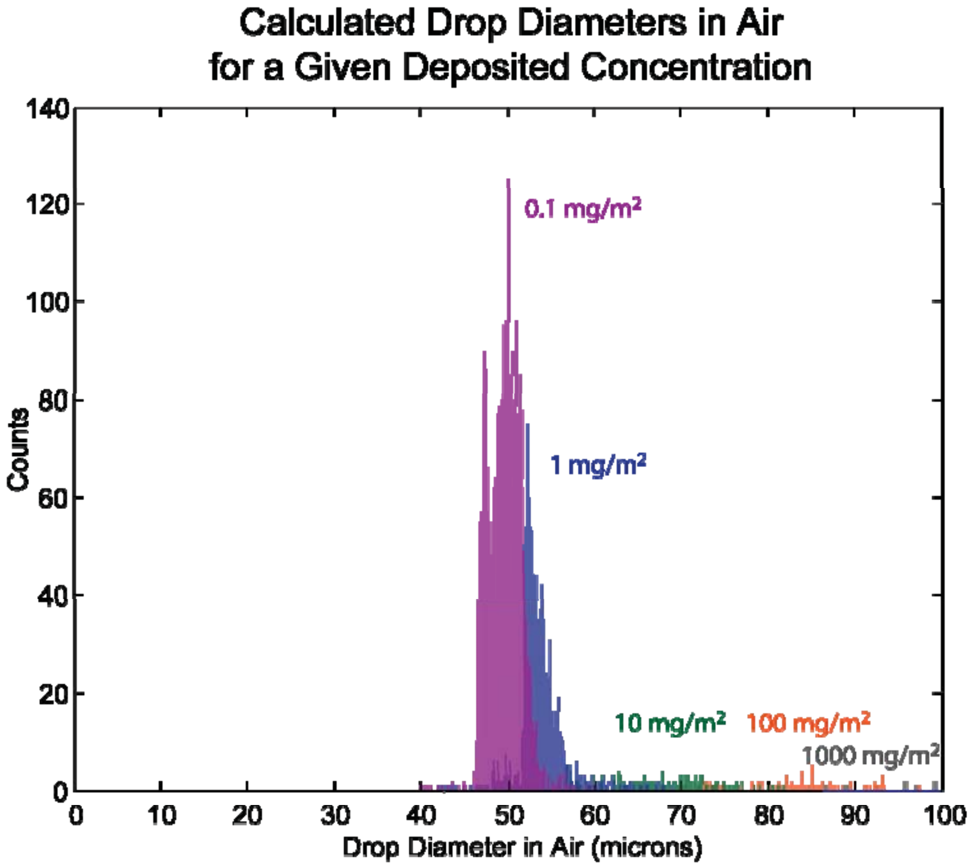
Calculated Drop Diameters in Air for a Given Deposited Concentration



- Areas of interest are those with concentration > 0.1 mg/m^2
- Average drop diameter in lowest concentration region is 500 μm

Maneuver: Drop Sizes




Calculated Drop Diameters in Air for a Given Deposited Concentration

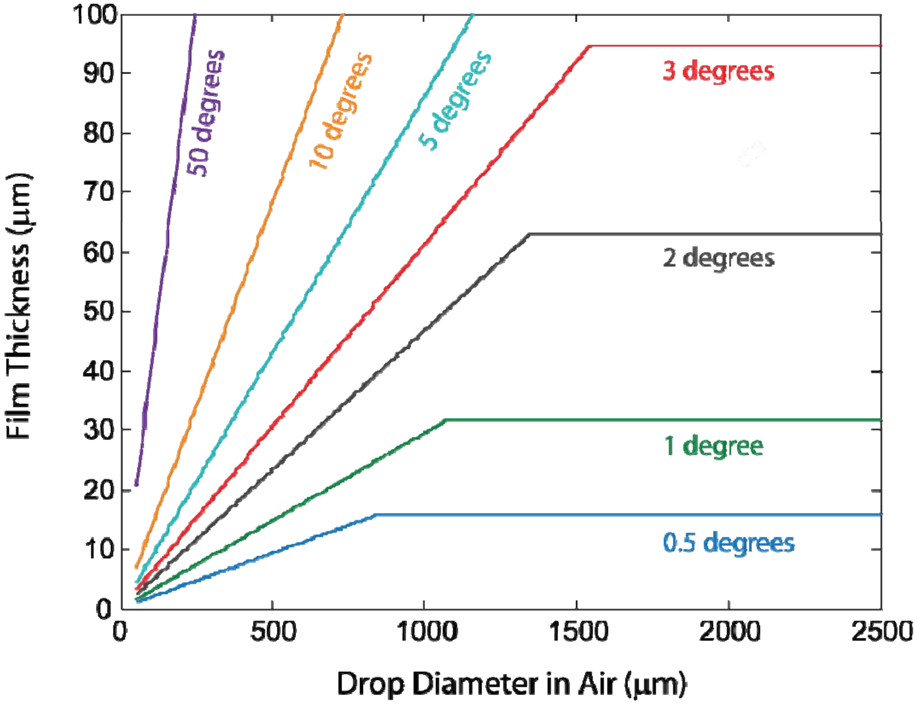
- Sprayers produce much smaller drop sizes than on the Fixed Site
- Average drop diameter in lowest concentration region is 50 μm

Drop and Film Characteristics

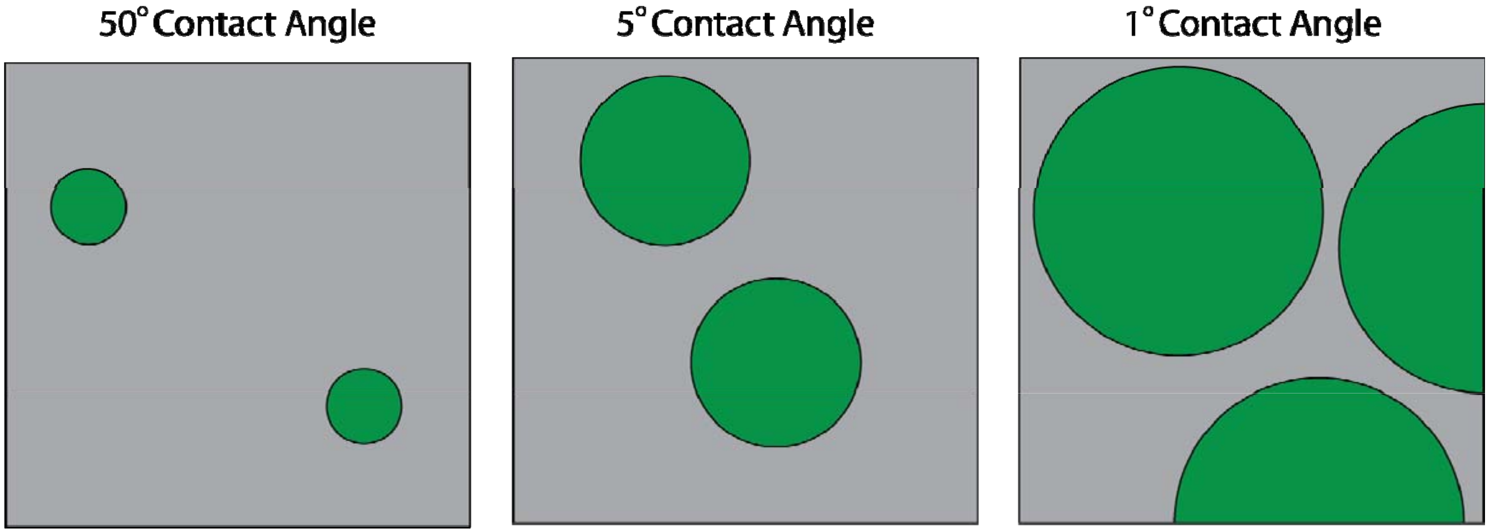
$$h_{EQ} = \sqrt{\frac{2\gamma\,(1 - \cos\theta_c)}{\rho g}}$$

- 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

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



Drop Spreading



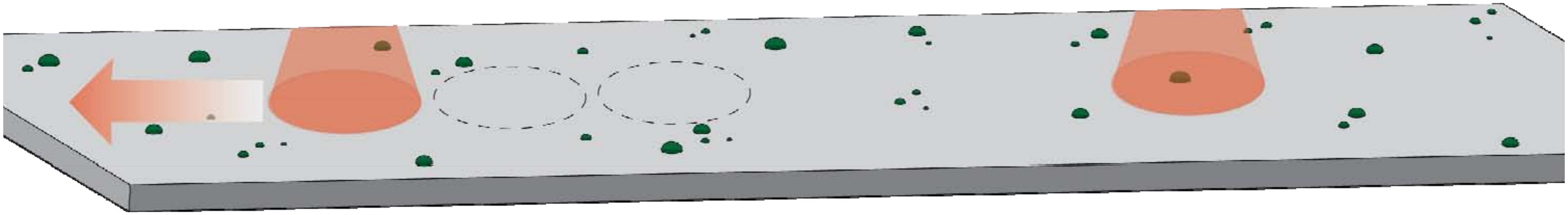
- Low contact angles will result in larger contaminant surface area, larger percentage of substrate covered in contaminant
- Wetting properties will vary between contaminants and between substrates
- Values are not readily available in the open literature, so contact angle is parameterized in this analysis

Probability of Detection (p_d)

System p_d is dependent on:

p_{drop}: Probability drop is interrogated

p_{sensor}: Probability sensor detects drop if interrogated



$$p_d = p_{drop} \cdot p_{sensor}$$

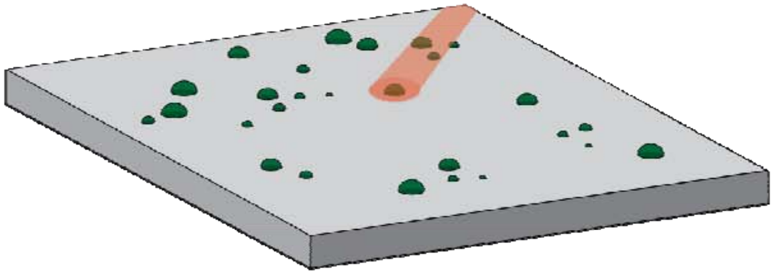
System $\mathbf{p_d}$ could be very poor even with a “perfect” sensor ($\mathbf{p_{sensor}}$ = 1)

Probability of Detection (p_d)

$$\boxed{p_d = p_{drop} \cdot p_{sensor}}$$

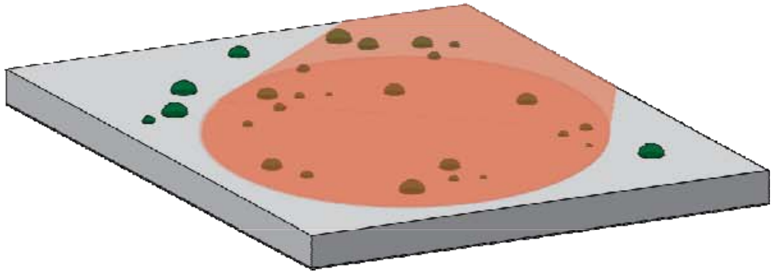
High Sensitivity
Low Area Coverage Rate
Low Probability of Encountering a Drop

p_{drop} ↓ p_{sensor} ↑

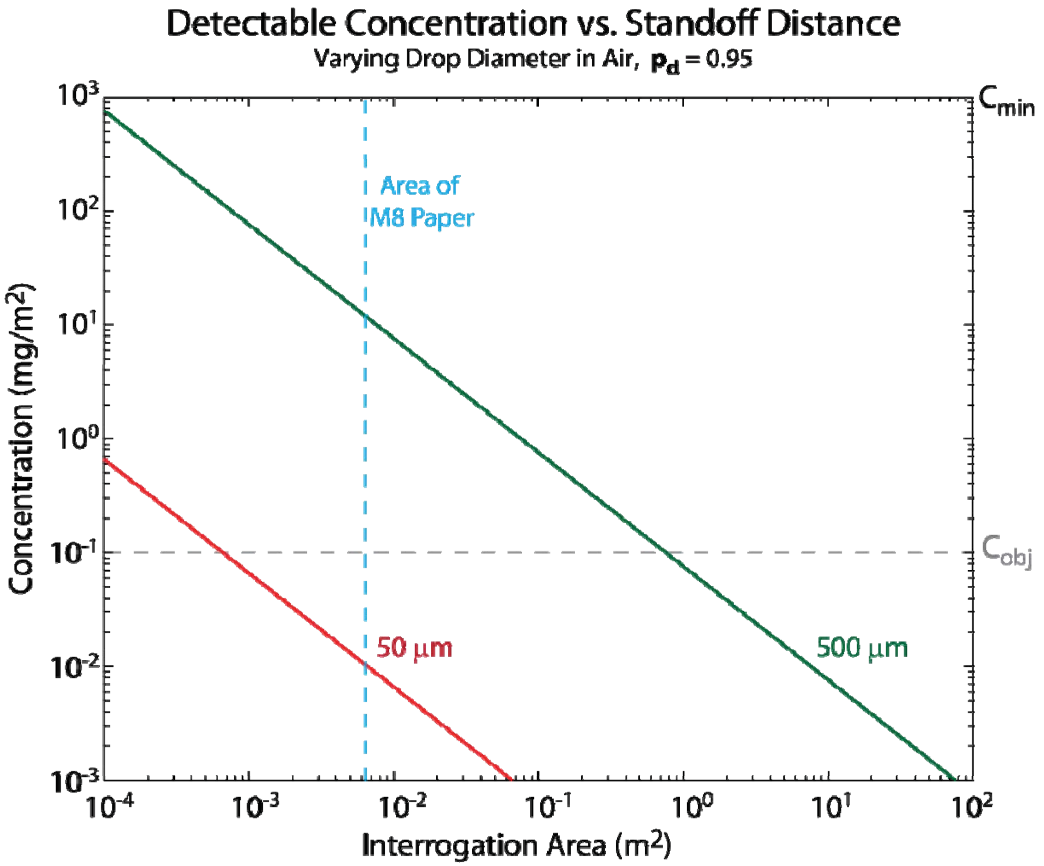


Lower Sensitivity
Higher Area Coverage Rate
Higher Probability of Encountering a Drop

p_{drop} ↑ p_{sensor} ↓



Choice of Interrogation Area



- Interrogation area required for a $\mathbf{p_d}$ 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 $\mathbf{p_d}$

Desired detection capability will define necessary size of interrogated area

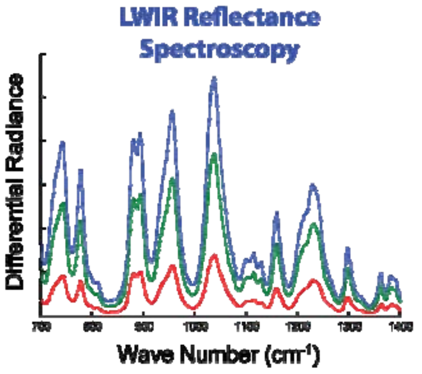
Outline

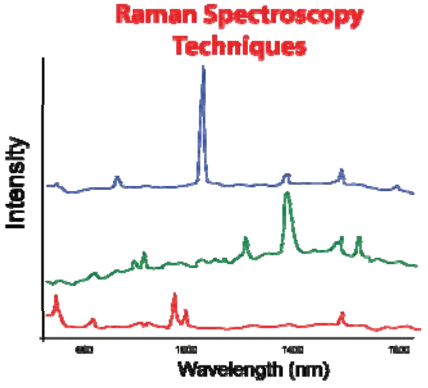
- **Example Mission Scenarios**
  - Current Technologies
  - Operational Requirements
  - Concentration Profiles
  - Contaminant Phenomenology
- **Potential Standoff Technologies**
- **Application to Scenarios: Fixed Site**
  - Raman Spectroscopy
  - Active and Passive LWIR Spectroscopy
- **Application to Scenarios: Maneuver**
  - Active and Passive LWIR Spectroscopy
- **Conclusions**

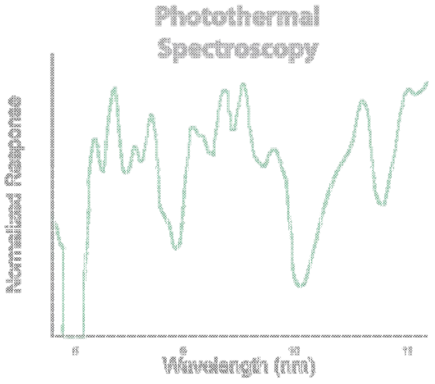
Potential Technologies for Standoff CWA Detection

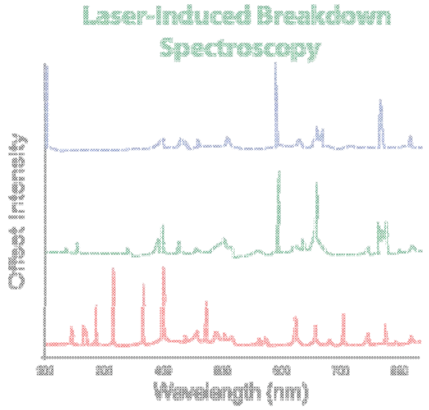
- Consider technologies that have been demonstrated to be capable of “true” standoff CWA detection
  - No sample collection
  - No special substrates required
  - Nothing but photons interacting with contaminant

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

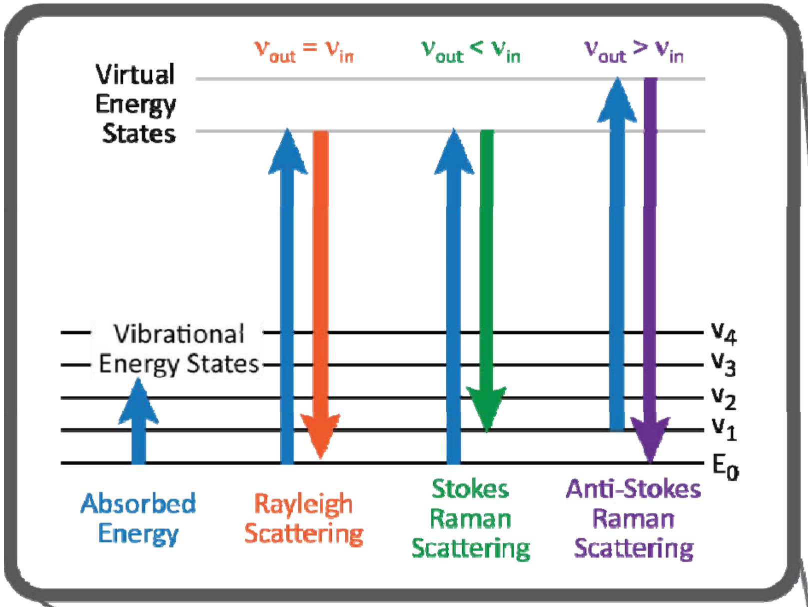




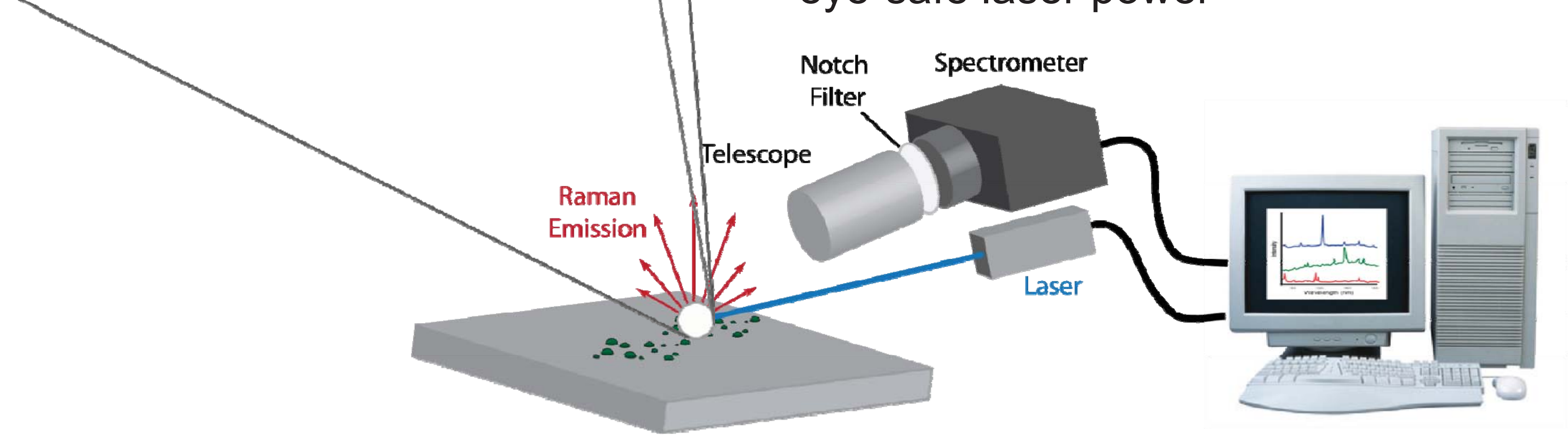




Potential Detection Technology: Raman



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



Optimizing Raman Signal: Importance of Deposition Details (VX)

Photons Detected → $N_{out} = \Omega N_{in} \sigma_R C_{eff}$

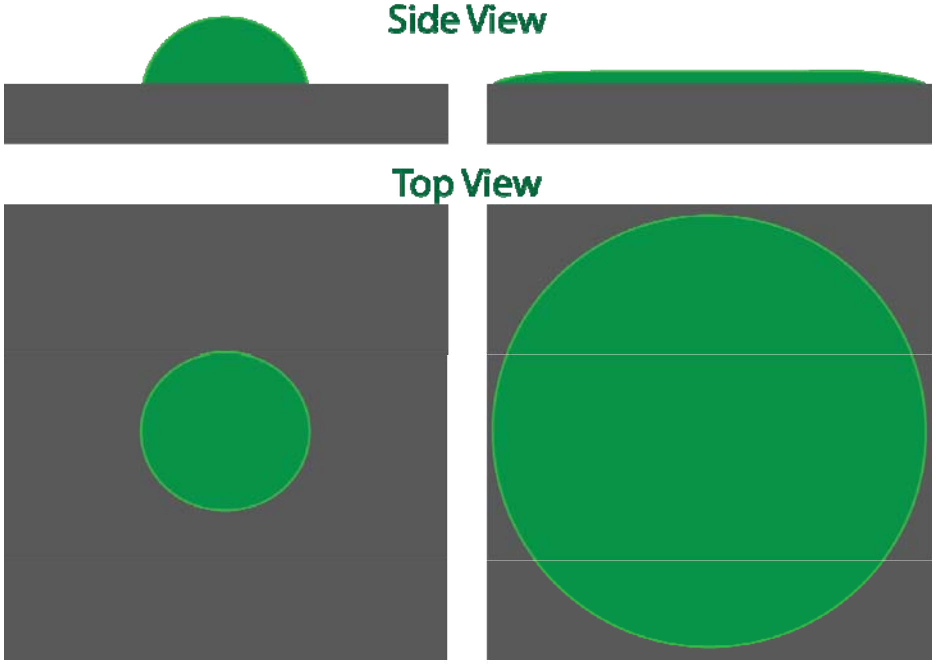
Solid Angle → Ω

Incident Photons → N_{in}

Raman Cross-Section → σ_R

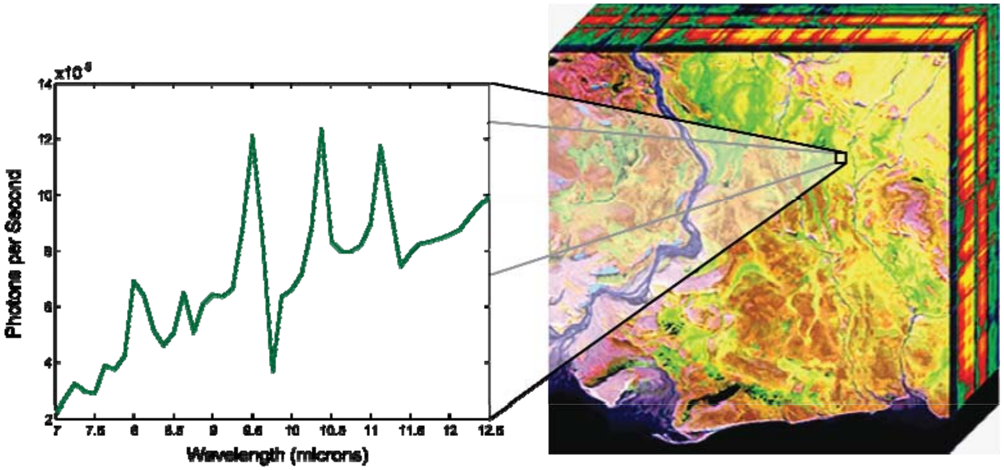
Contaminant Concentration → C_{eff}

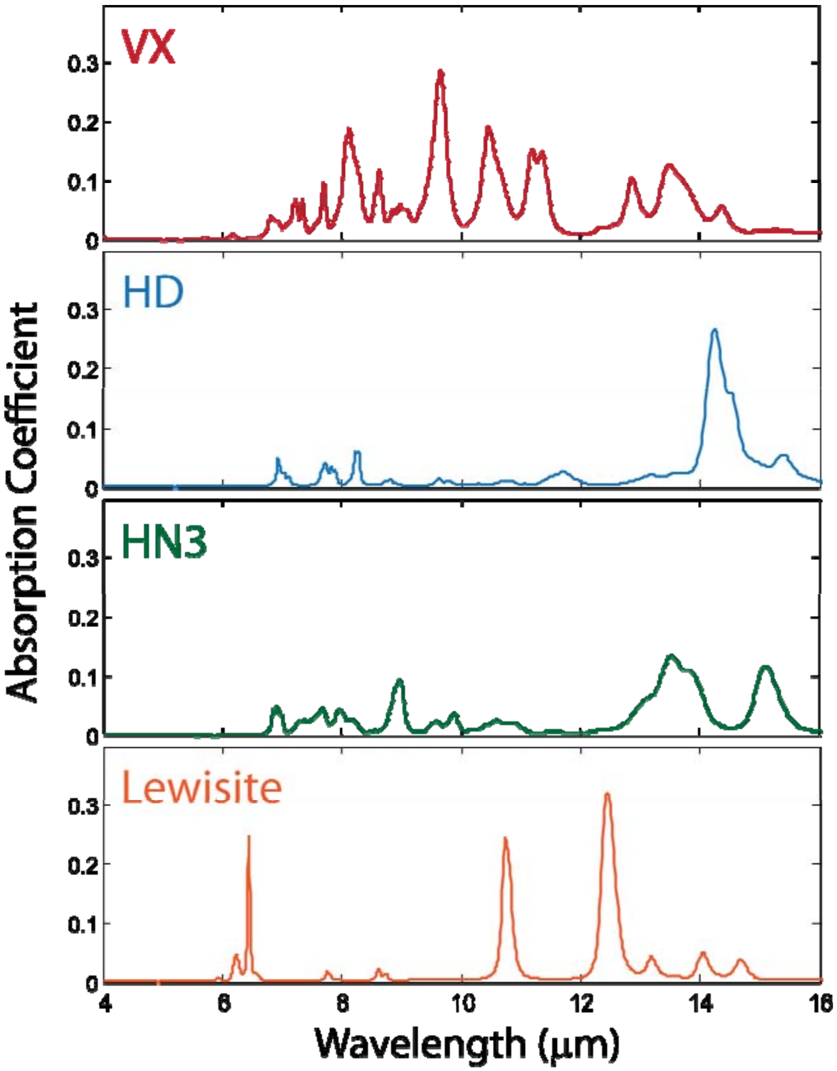
- For wavelengths at which VX absorbs strongly (e.g. deep UV), only the first micron of molecules is expected to contribute to Raman signal
- Same **volume** can have very different **surface area** depending on wetting



Potential Detection Technology: LWIR Reflectance

- CWAs have strong absorption features in the LWIR, which also coincides with atmospheric window
- Acquire reflectance data *vs.* λ either at a single point or at each pixel in a hyperspectral image to map out contamination
- Active or Passive techniques can be used

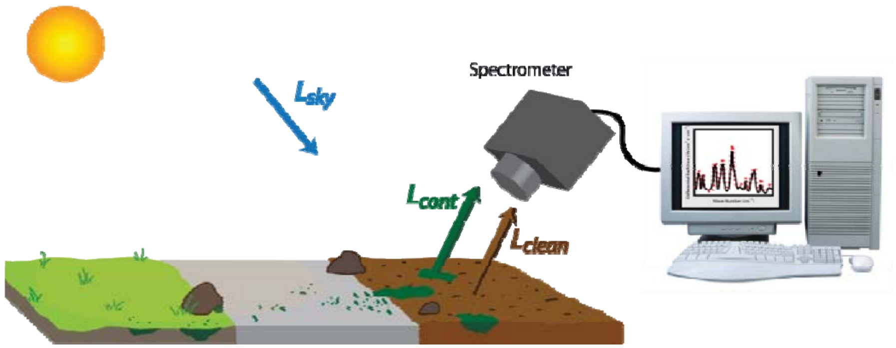




Potential Detection Technology: Passive and Active LWIR Reflectance

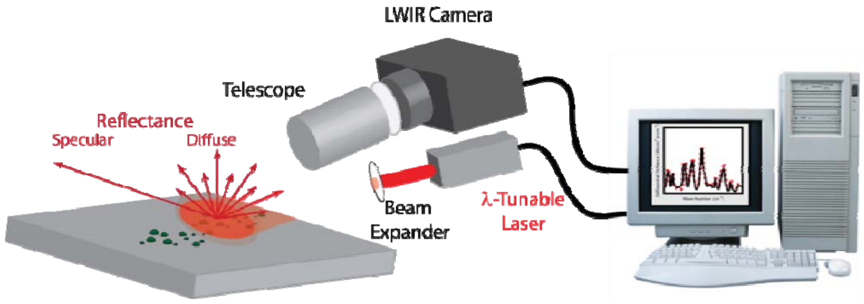
Passive

- 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

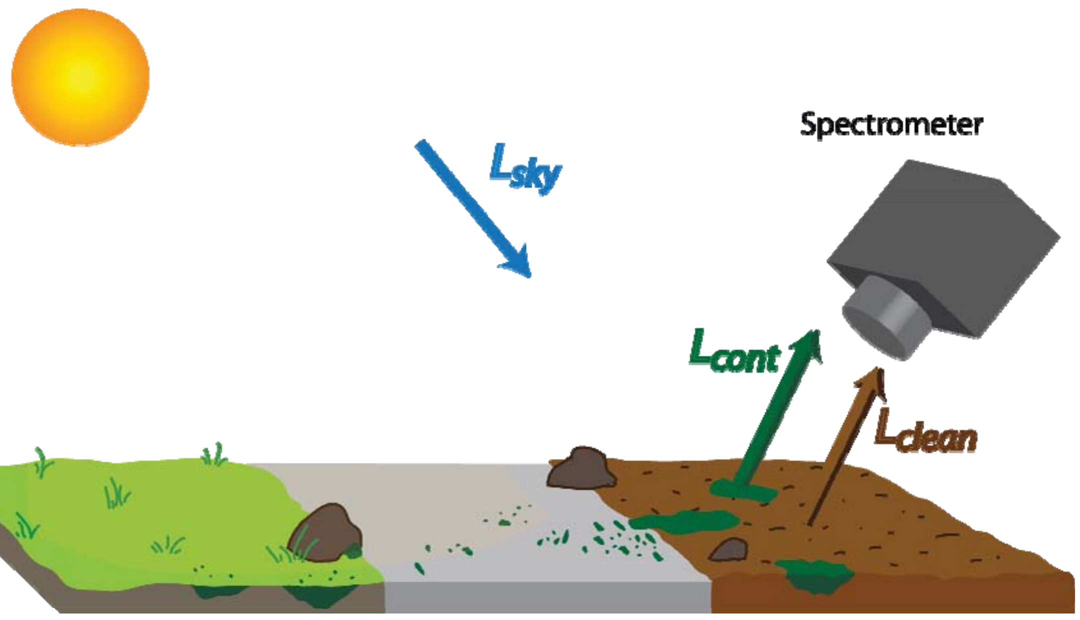


Active

- 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



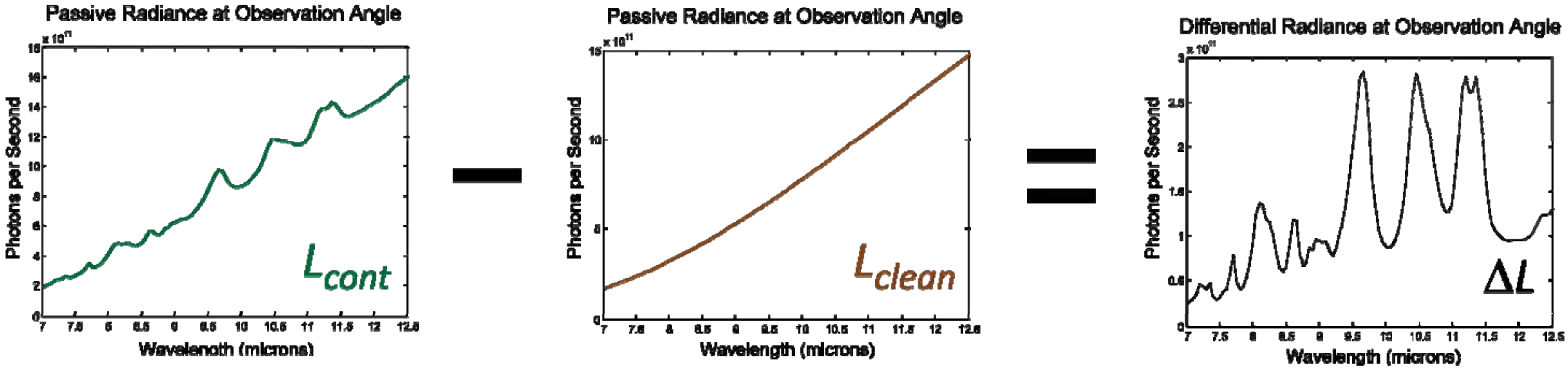
$$L_{clean} = B - R_{surf}(B - L_{sky})$$

$$L_{cont} = B - R_{cont}(B - L_{sky})$$

$$B = \frac{2hc^2\nu^3}{\exp(hc\nu/kT) - 1}$$ (Planck Radiance of surface)

Differential Radiance:

$$\Delta L = (R_{surf} - R_{cont})(B - L_{sky})$$

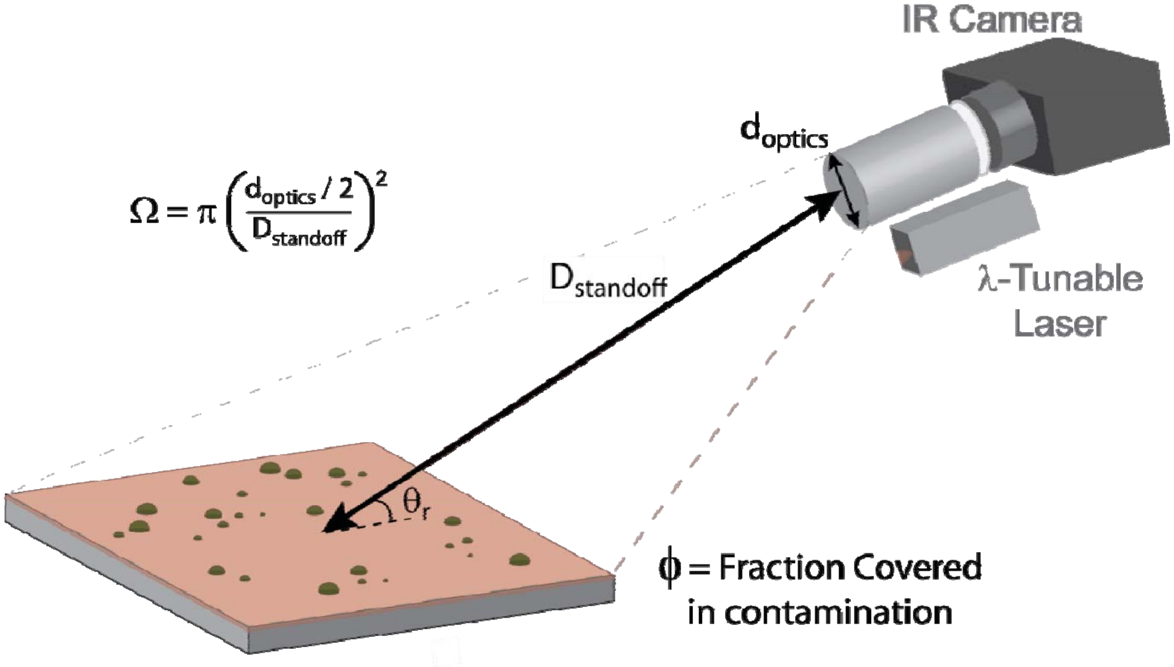


Active LWIR Signal Equations

User-Controlled

System Properties

R_{cont}



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

User-Controlled Parameters:

- Laser power ($\mathbf{P}_{laser}$) limited by SWaP, eye-safety
- Interrogation time (τ) limited by mission time constraints
- Solid angle (Ω) limited by required standoff distance, size constraints on optics

Signal Equations: Reflectivity

$$R_{cont} = (\rho_{cont})(\rho_{cont}^{*})$$

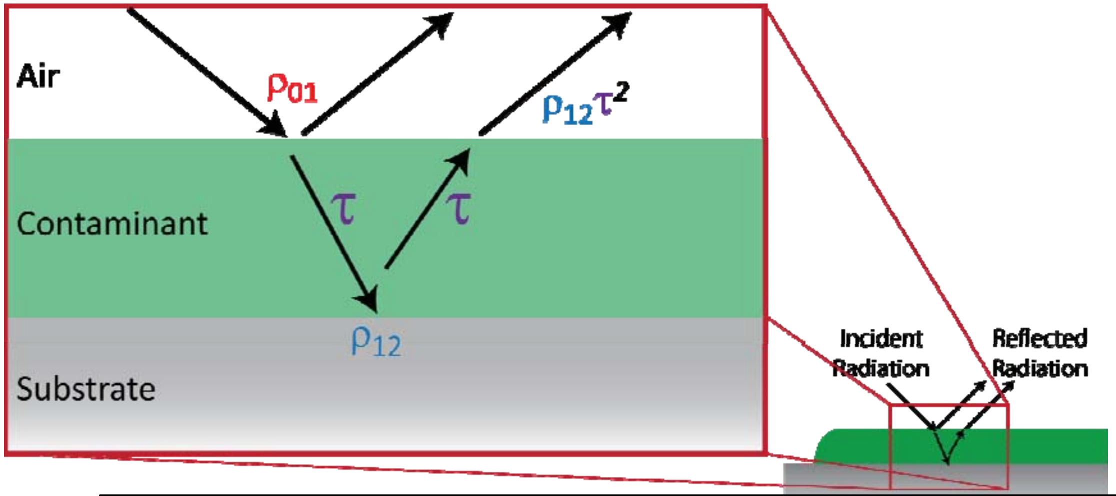
$$\text{where} \quad \rho_{cont} = \frac{\rho_{01} + \rho_{12}\tau^2}{1 + \rho_{01}\rho_{12}\tau^2}$$

ρ_{01} = Air-Contaminant Interface Reflectance Amplitude

ρ_{12} = Contaminant-Substrate Interface Reflectance Amplitude

τ = Contaminant Single-Pass Transmission

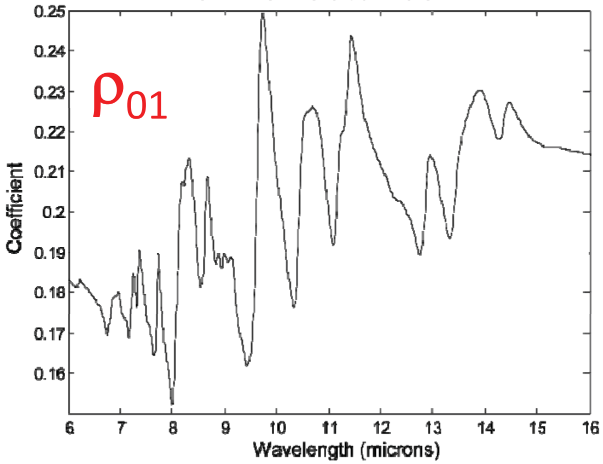
- Substrate reflectivity (ρ_{12}) scales double-pass transmission (τ^2)
- For a minimally reflective substrate, the air-contaminant reflectance amplitude (ρ_{01}) will dominate
- For a highly reflective substrate with sufficient transmission, absorption features from the double-pass transmission will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



Reflectance properties are a function of both **substrate** and **contaminant** properties, and determine **signal quality** at detector

Transmission and Reflectance Coefficients (VX Example)

Front Face Amplitude of Reflectance

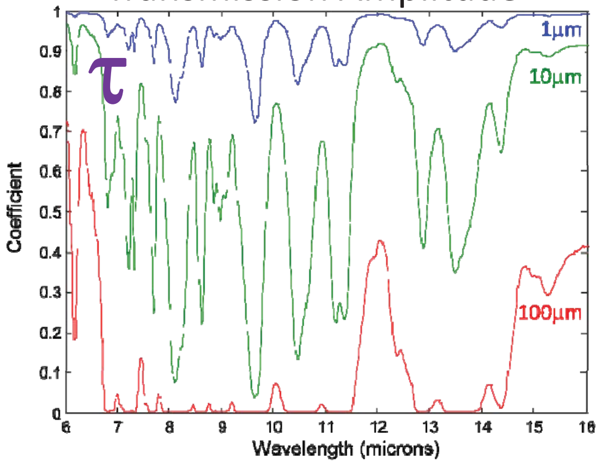


$$R_{cont} = (\rho_{cont})(\rho_{cont}^{*})$$

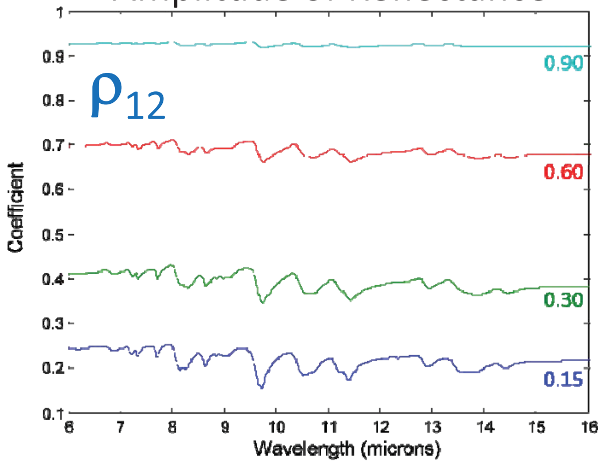
where $$\rho_{cont} = \frac{\rho_{01} + \rho_{12}\tau^2}{1 + \rho_{01}\rho_{12}\tau^2}$$

- Absorption spectral features (seen in τ) become less clear as film thickness increases
- Front face reflectance amplitude (ρ_{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

Single-pass Transmission Amplitude

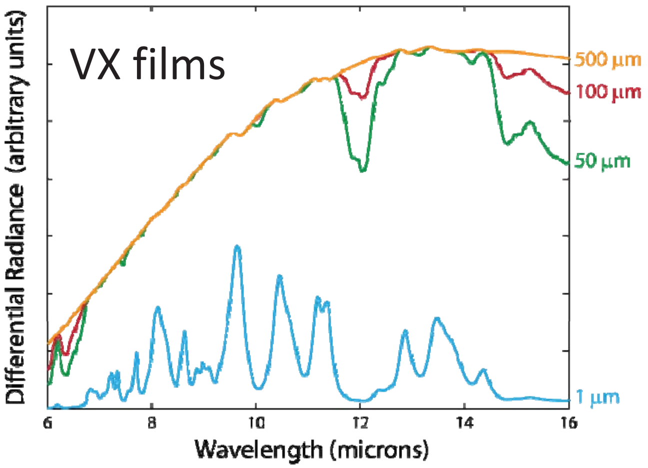


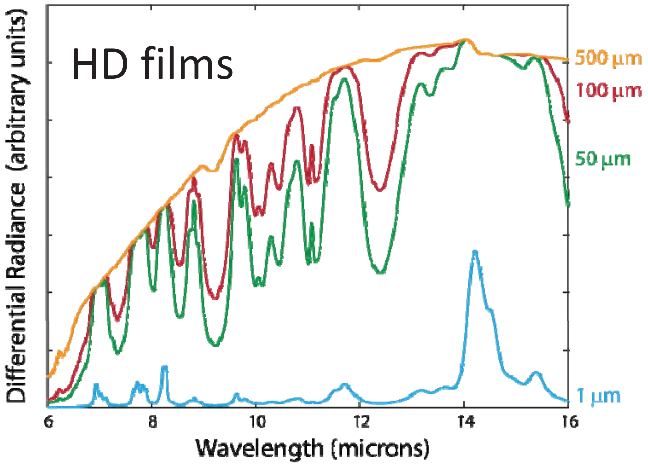
Substrate-Contaminant Amplitude of Reflectance



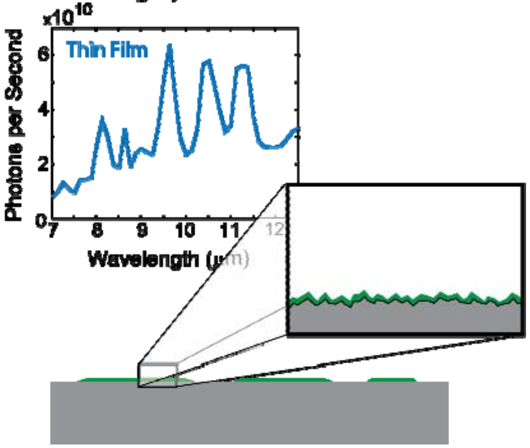
Detection Capabilities and Contaminant Distribution: Signal Quality

Signal can be **strong**, but without clear spectral features and thus **low-quality**

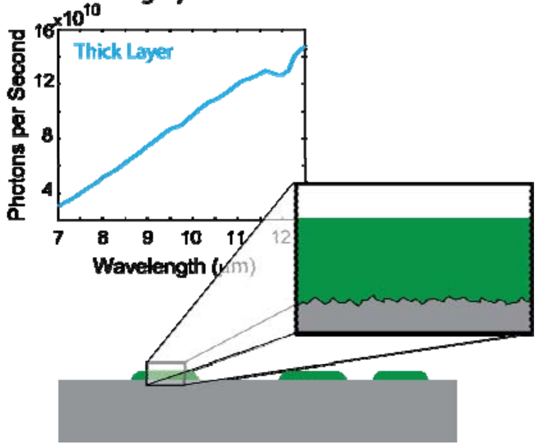




Thin VX Film on a
Highly Reflective Substrate



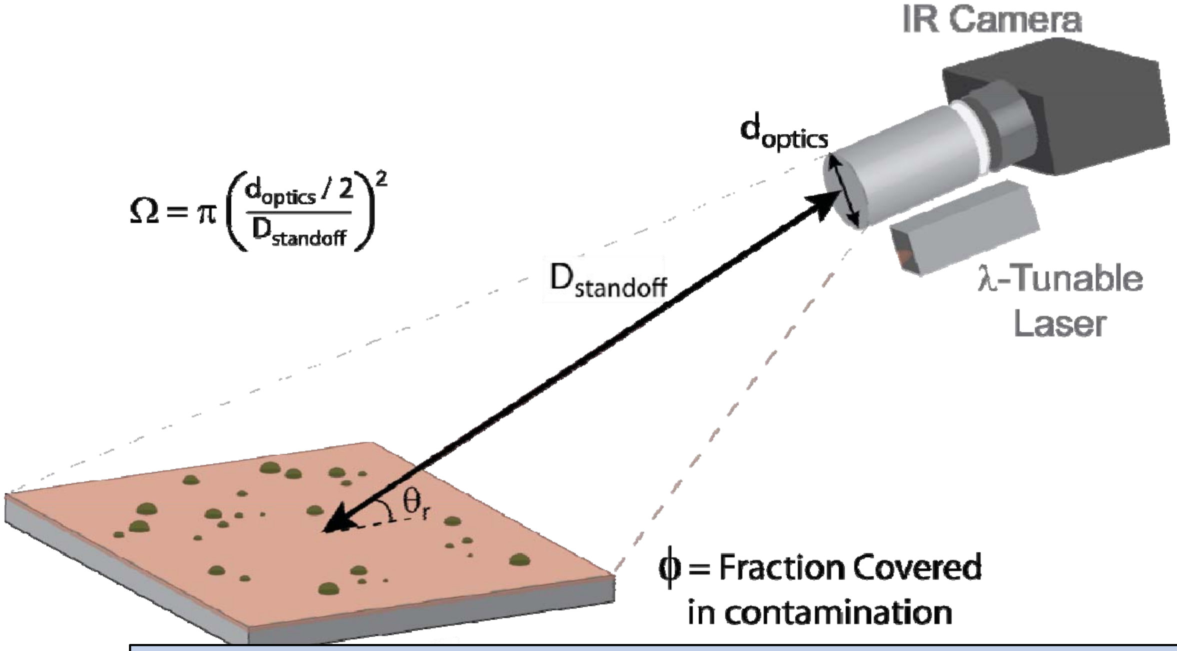
Thick VX Film on a
Highly Reflective Substrate



Active LWIR Signal Equations: Scattering Properties

$$N_{cont} = \overbrace{P_{laser} \cdot \tau \cdot \Omega}^{\text{User-Controlled}} \cdot \overbrace{f_{BRDF} \cdot [(1-\phi) \cdot R_{clean} + \phi \cdot R_{cont})]}^{\text{System Properties}}$$

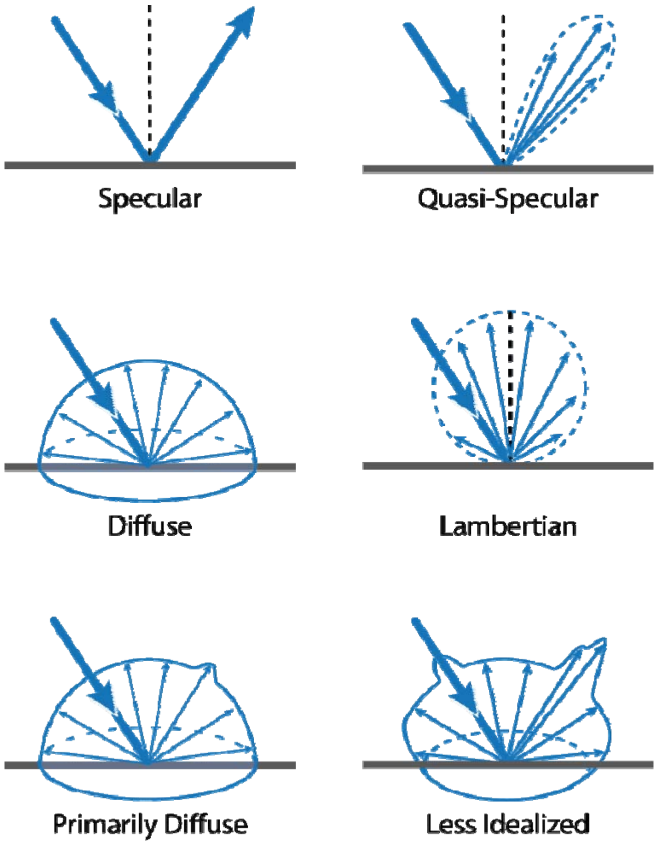
$$N_{clean} = \overline{P_{laser} \cdot \tau \cdot \Omega} \cdot \overline{f_{BRDF} \cdot R_{clean}}$$



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

ϕ = Fraction Covered in contamination

Scattering Profiles (f_{BRDF})



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

Outline

- **Example Mission Scenarios**
  - Current Technologies
  - Operational Requirements
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  - Raman Spectroscopy
  - Active and Passive LWIR Spectroscopy
- **Application to Scenarios: Fixed Site**
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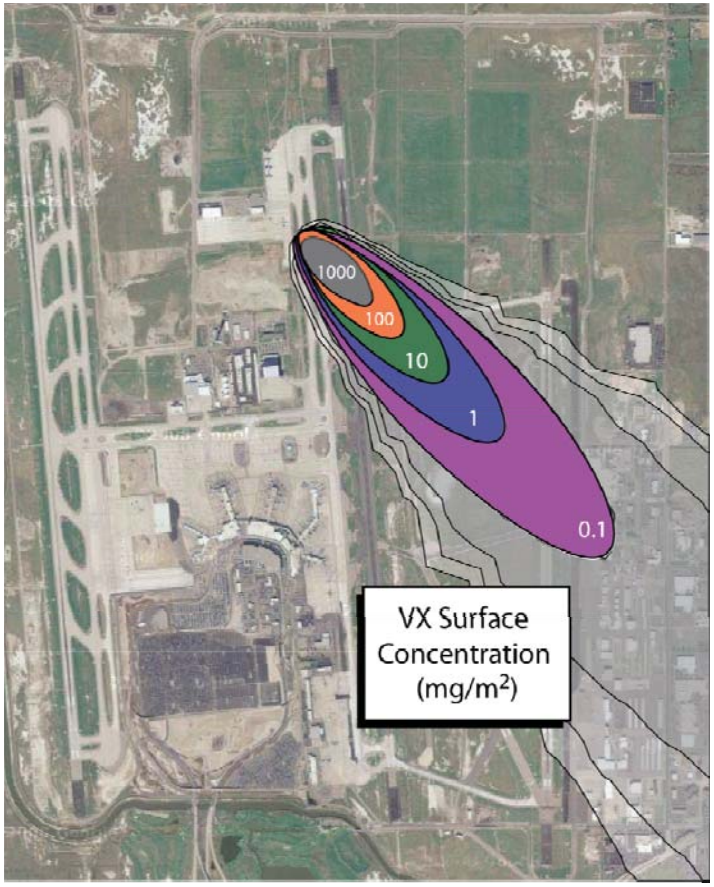
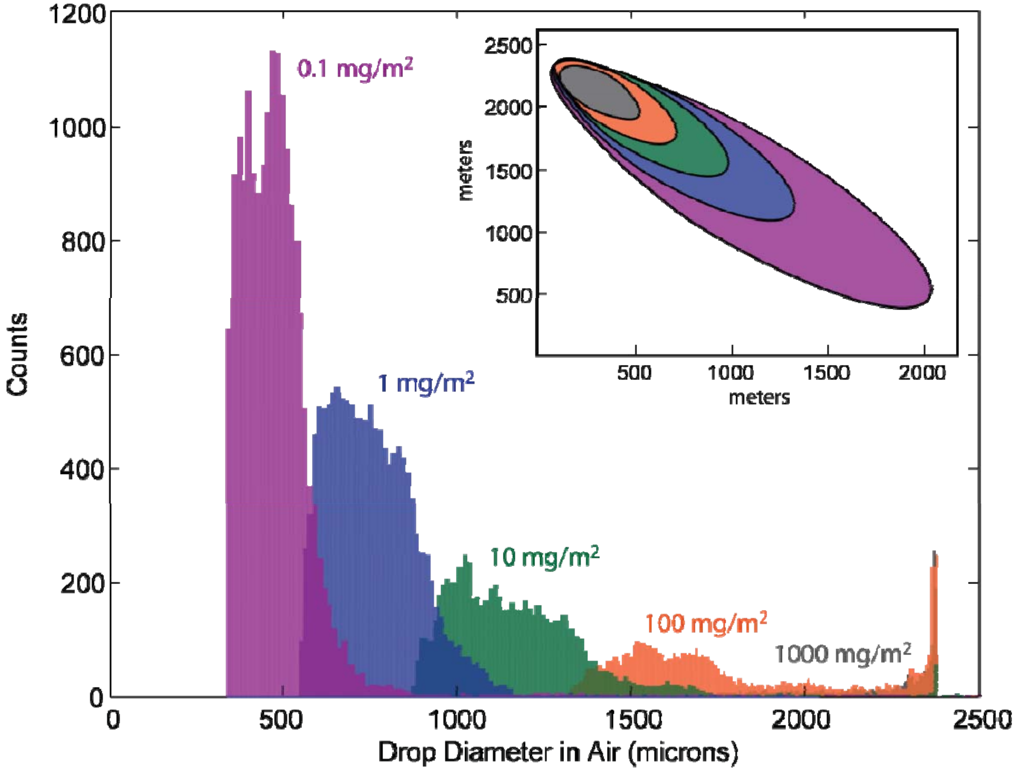
- **Application to Scenarios: Maneuver**
  - Active and Passive LWIR Spectroscopy
- **Conclusions**

Fixed Site

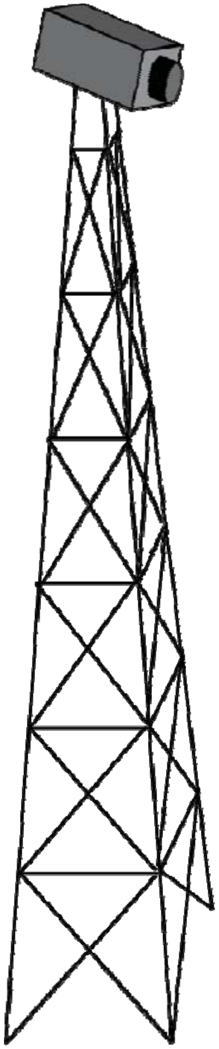


Calculated Drop Diameters in Air for a Given Deposited Concentration

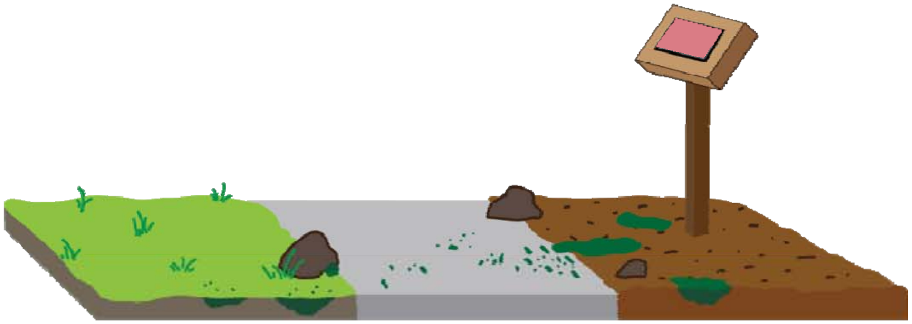


- Baseline Technology: **M8 Paper**
- Can take advantage of fixed site by pre-placing cooperative or carefully chosen substrates around the base

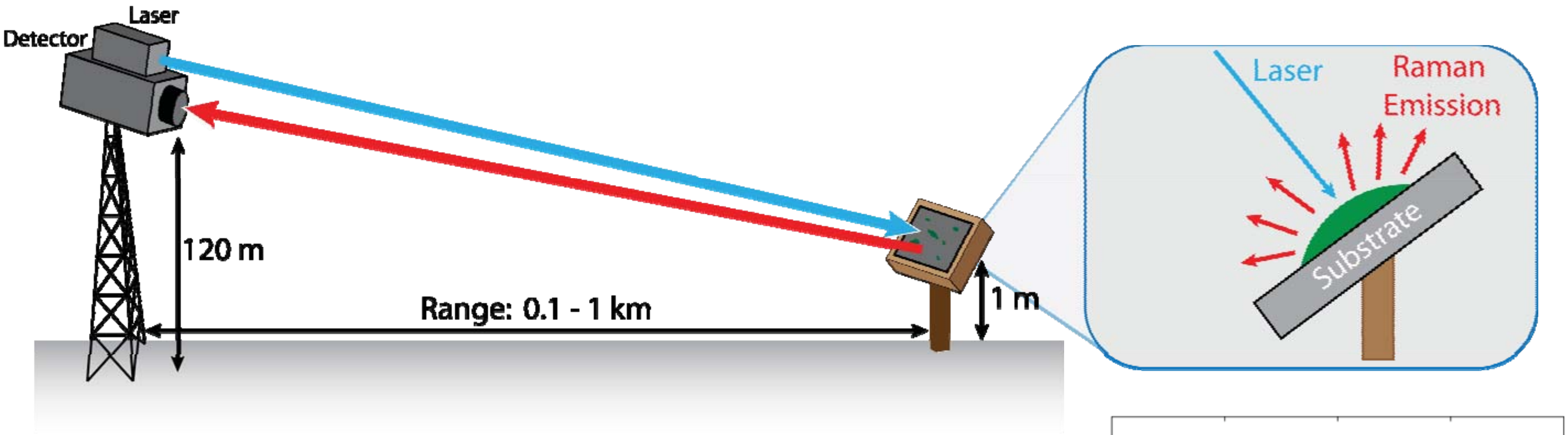
Fixed Site:
Tower Platform w/ Stands



- 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



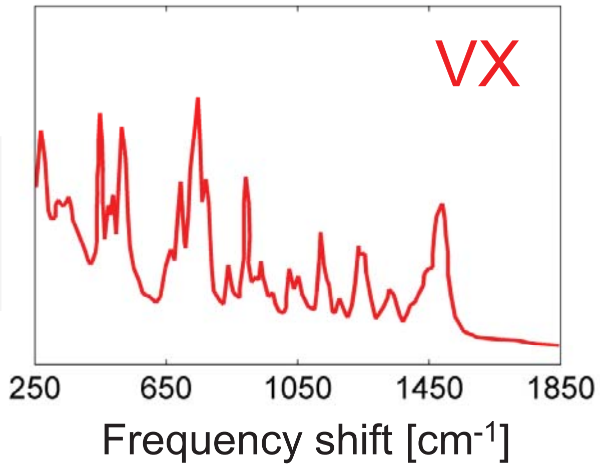
Raman Setup



Agent	785 nm	248 nm	
	σ_R [1]	σ_R [2]	T_{max} (μm)
GB	1.2	360	540
VX	1.0	2,500	1.0
HD	3.0	4,800	8.4

[1] 10^{-30} cm^2 sr^{-1} molecule^{-1}
[2] Christesen, SPIE (2006)

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



Analysis will focus on Raman excitation in UV region (λ = 248nm)

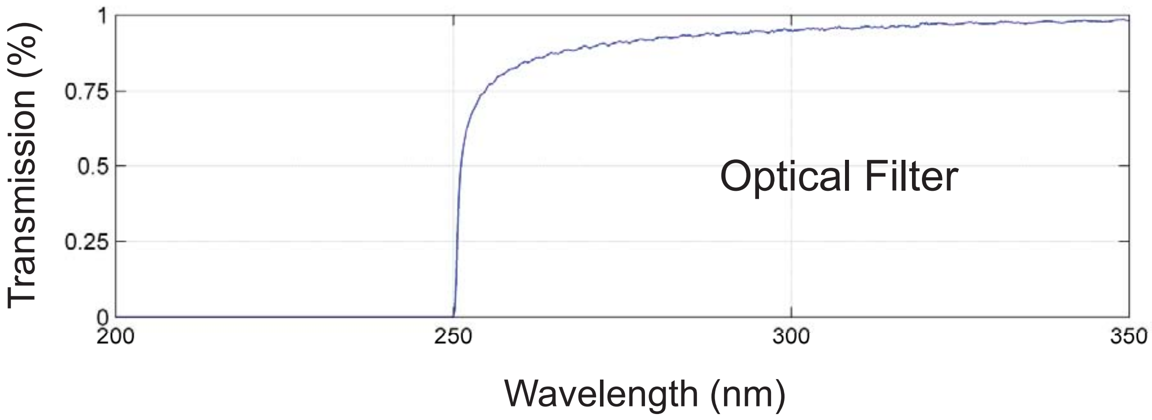
UV Raman Analysis

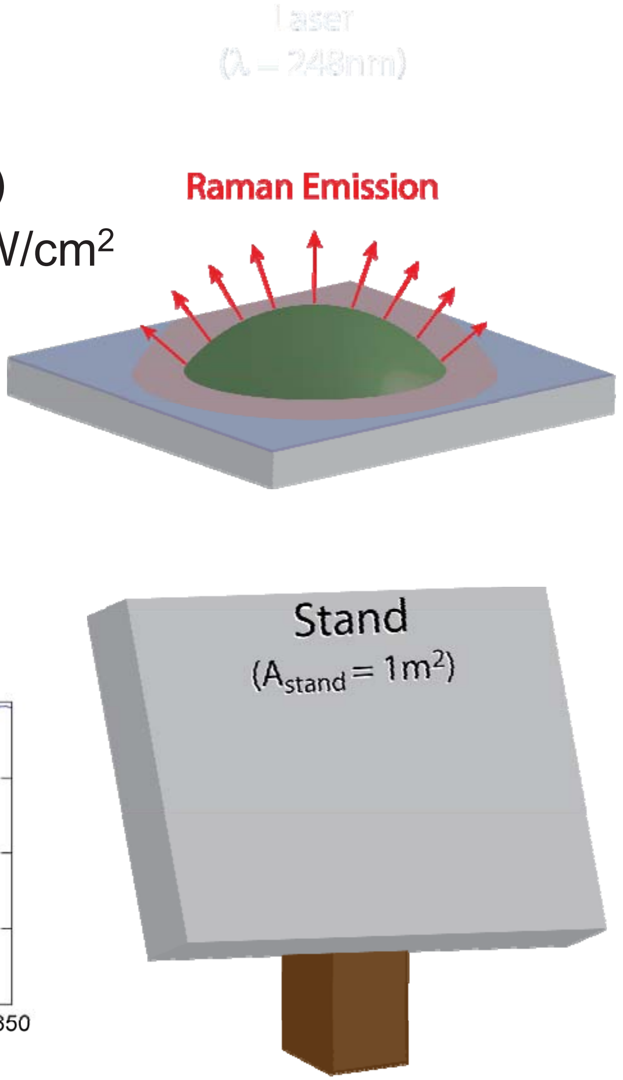
Transmit:

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

Receive:

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





UV Raman Analysis

Signal Model:

$$e^{-}_{255} = \mathbf{QE} \cdot \Omega \cdot \tau \cdot \mathbf{P}_{\mathbf{laser}} \cdot \sigma_{\mathbf{R}} \cdot \frac{\text{Molecules}}{\mathbf{A}_{\mathbf{stand}}}$$

Where:
QE = Detector Quantum Efficiency
Ω = Solid angle (sr)
τ = integration time (seconds)
P_{laser} = Laser power in photons per second
σ_R = VX Raman cross-section = 2.5×10^{-27} cm^2/molecule
A_{stand} = 1 m^2

$$\text{Molecules} = N_{drop} \cdot SA_{drop} \cdot t_p$$

Where:
N_{drop} = Number of drops on stand
SA_{drop} = Surface Area of individual drop
t_p = penetration depth at 248nm in VX = 1μm

Signal + Noise Model:

Noise Sources:

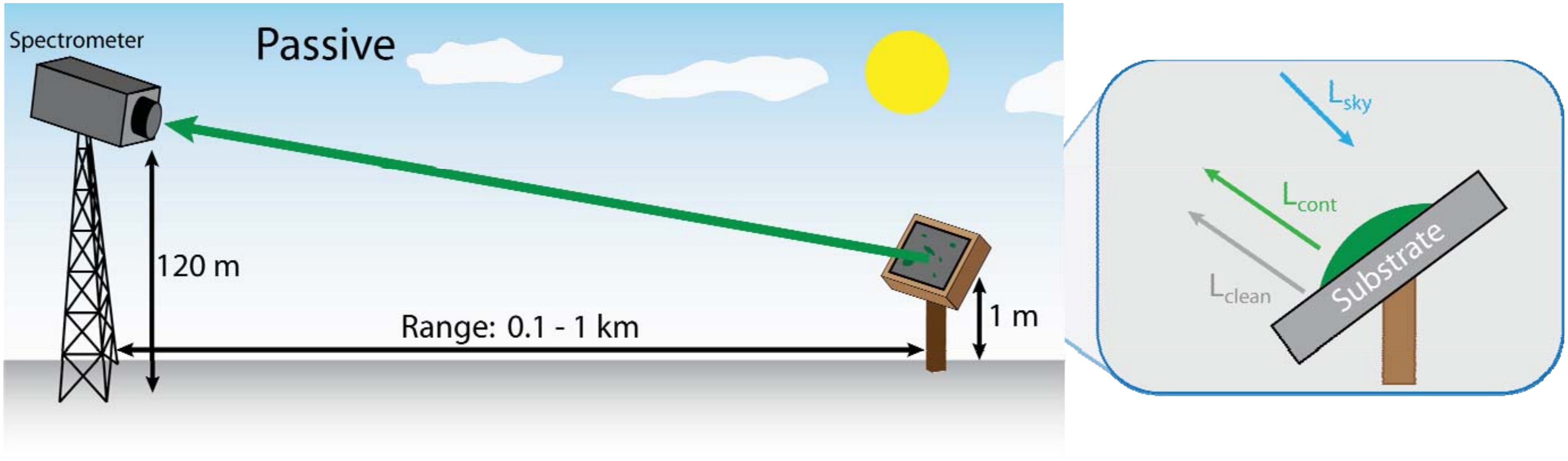
- Shot Noise
- Detector Dark Noise
- Readout Noise

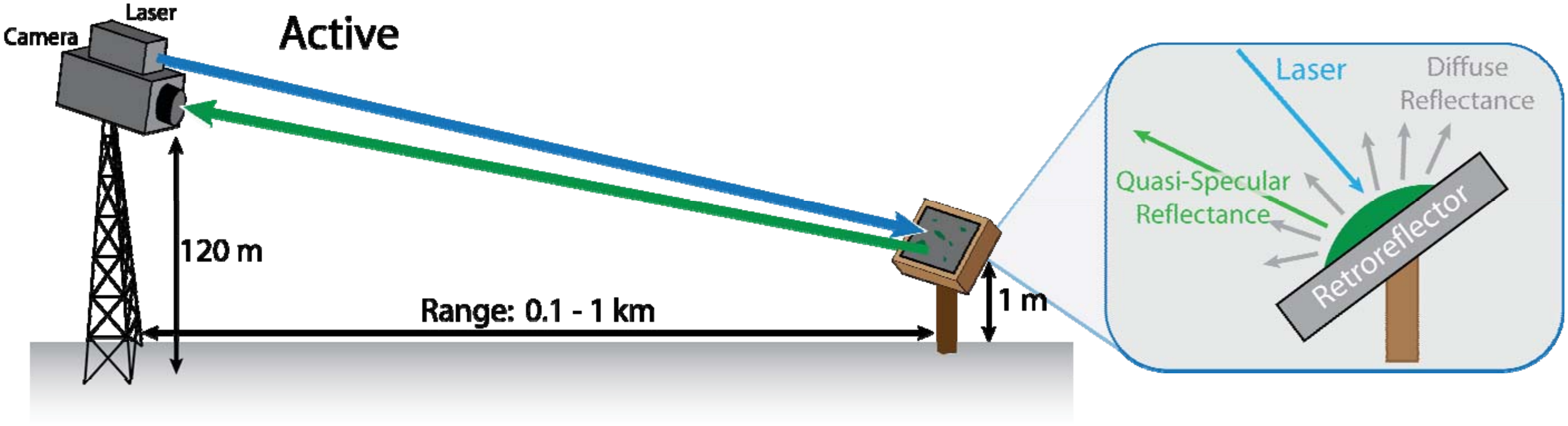
$$\mu_{signal} = e^{-}_{255} + e^{-}_{\text{Dark Noise}} + e^{-}_{\text{Read Noise}}$$

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

Simple detection algorithm: If $\mu_{signal} \geq$ threshold → ALARM

Active and Passive LWIR Setup





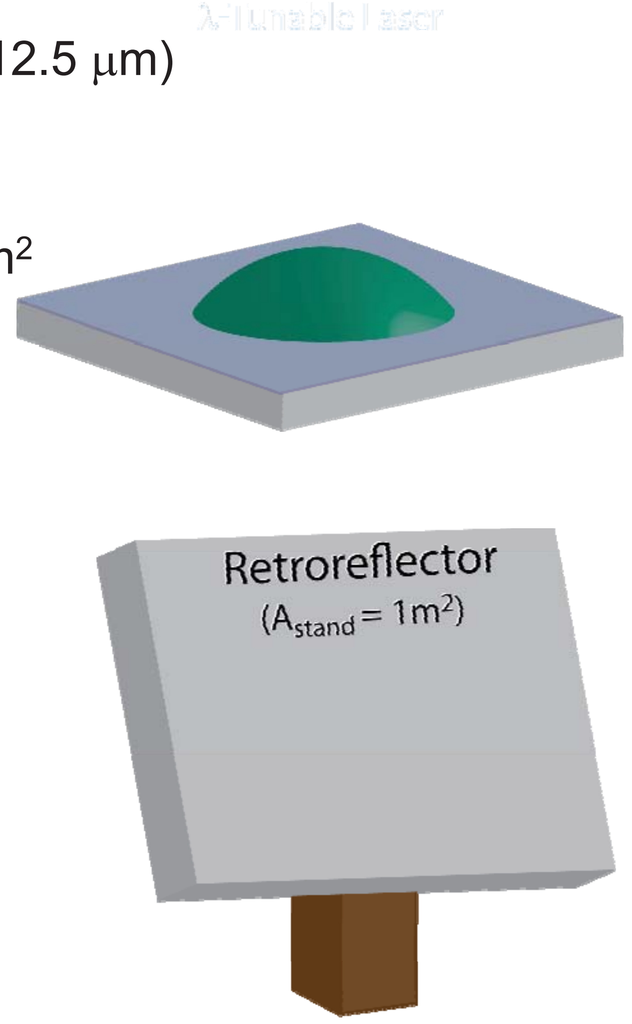
Active LWIR Analysis

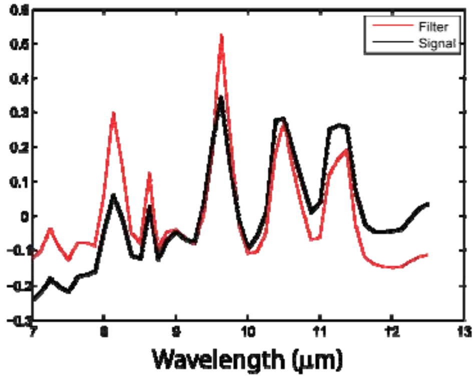
Transmit:

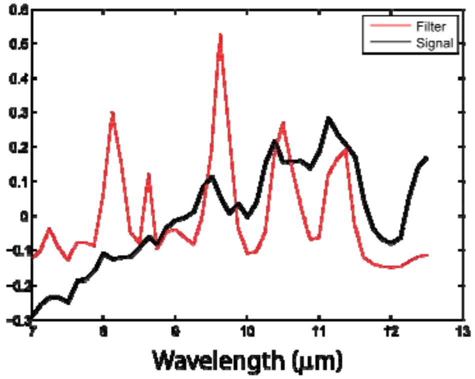
- Illuminate retroreflector w/ tunable laser ($\lambda = 7.0–12.5\ \mu m$)
- 437 stands interrogated in 25 minutes ($\tau = 3.5s$)
- Signal-average 50 times during τ
- Eye Safe Power (λ in LWIR, $\tau = 3.5s$): 219 mW/cm^2

Receive:

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







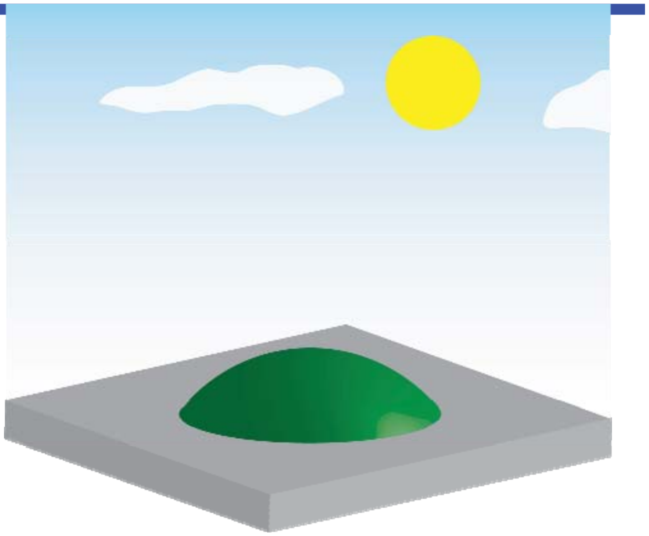
Passive LWIR Analysis

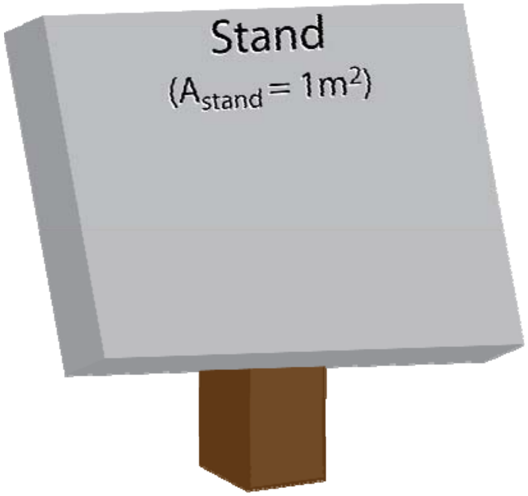
Transmit:

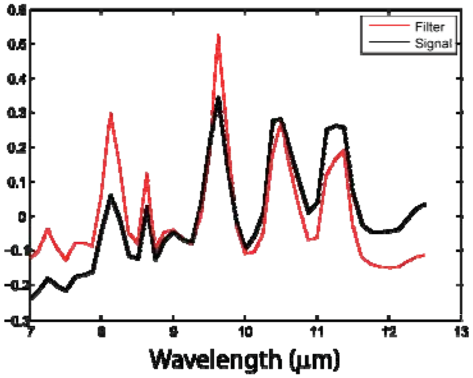
- 437 stands interrogated in 25 minutes ($\tau = 3.5$s)
- Assume 50° ΔT between substrate and sky
- Treat substrate and sky as black bodies

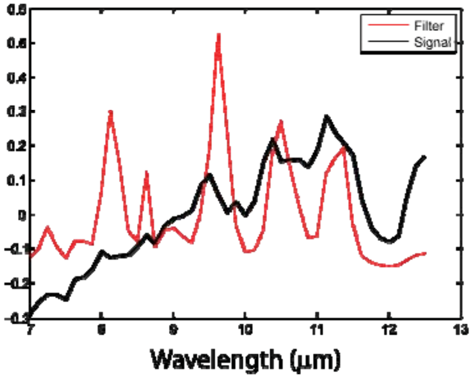
Receive:

- Assume entire stand is one pixel
- Clean signal subtracted from contaminated
- Spectral signature compared to matched filter









LWIR Analysis

Signal Model:

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

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

Where:
QE = Detector Quantum Efficiency
Ω = 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:

$$\mu_{signal} = \mathbf{e}^{-}_{255} + \mathbf{e}^{-}_{dark}$$

$$\sigma_{signal} = \sqrt{\mu_{signal}}$$

Noise Sources:

- Shot Noise
- Detector Noise

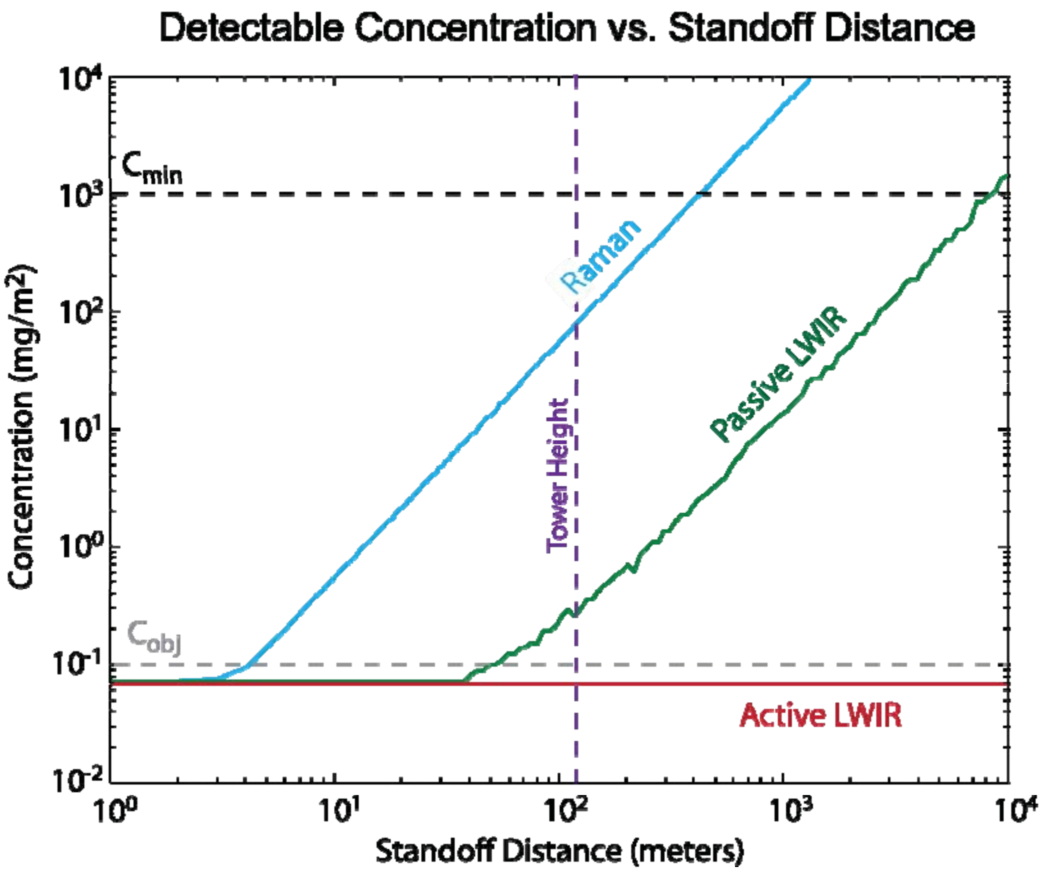
$$\alpha_{filter} = \text{VX absorption matched filter}$$

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

$$\text{mf}_{signal} = \frac{\mu_{signal} \cdot \alpha_{filter}}{\sqrt{(\mu_{signal} \cdot \mu_{signal})(\alpha_{filter} \cdot \alpha_{filter})}}$$

Matched filter algorithm: If $\text{mf}_{signal} \geq$ threshold → ALARM

Fixed Site: Performance Curves


Detectable Concentration vs. Standoff Distance

- **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

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

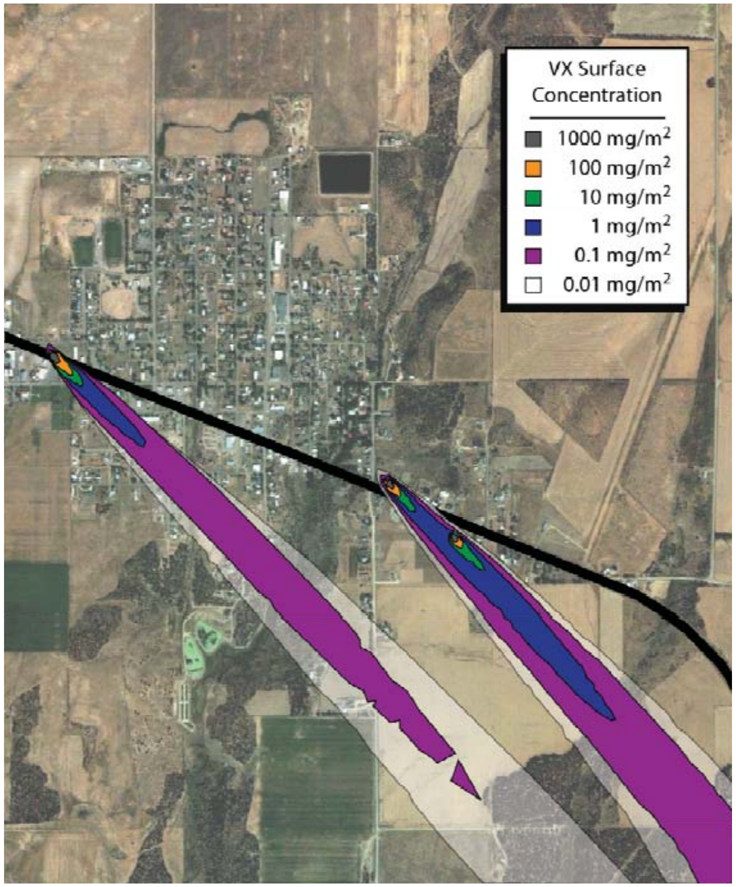
- Standoff Spot Detection
  (e.g. UV Raman on Ground Vehicle)
  - ID with high specificity from 10s of meters in area indicated by wide area sensor

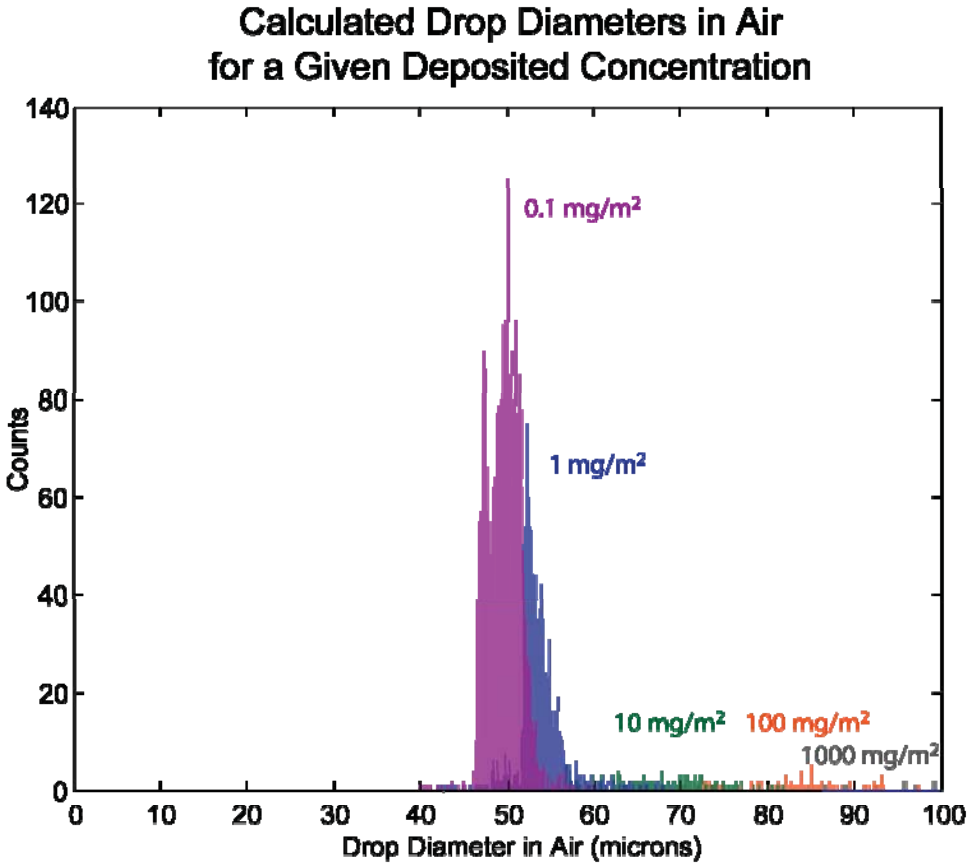
- Short-Range Spot Detection
  (e.g. Raman and/or LIBS on UGV)
  - Detect and ID lower levels of contamination with high sensitivity

Outline

- **Example Mission Scenarios**
  - Current Technologies
  - Operational Requirements
  - Concentration Profiles
  - Contaminant Phenomenology
- **Potential Standoff Technologies**
  - Raman Spectroscopy
  - Active and Passive LWIR Spectroscopy
- **Application to Scenarios: Fixed Site**
  - Raman Spectroscopy
  - Active and Passive LWIR Spectroscopy
- **Application to Scenarios: Maneuver**
  - Active and Passive LWIR Spectroscopy
- **Conclusions**

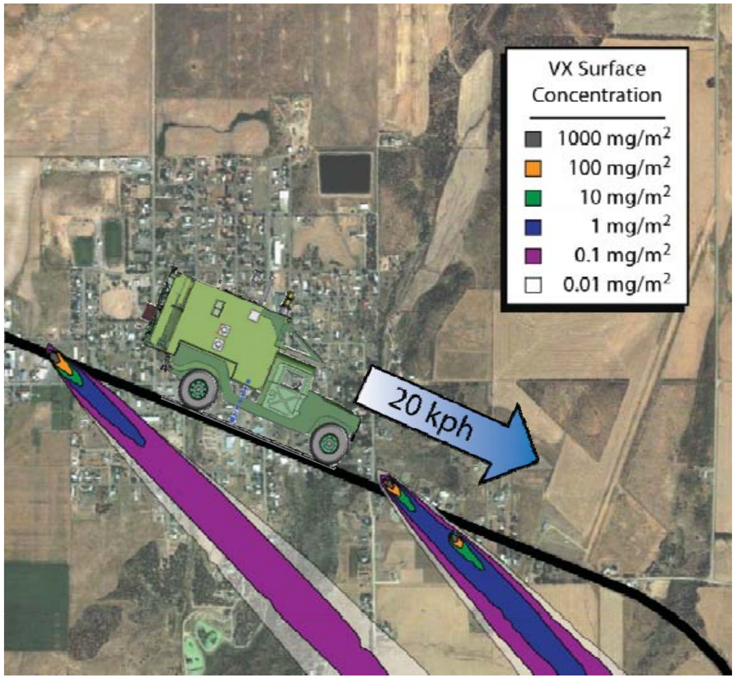
Maneuver

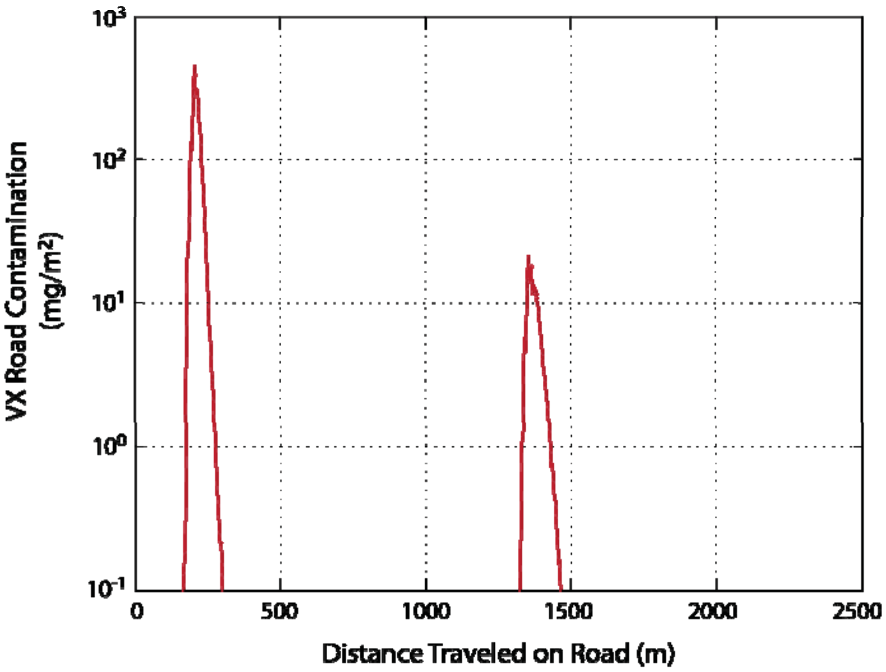




- Baseline Technology: **JCSD**
- Will attempt larger interrogation area, standoff detection

Concentration Encountered





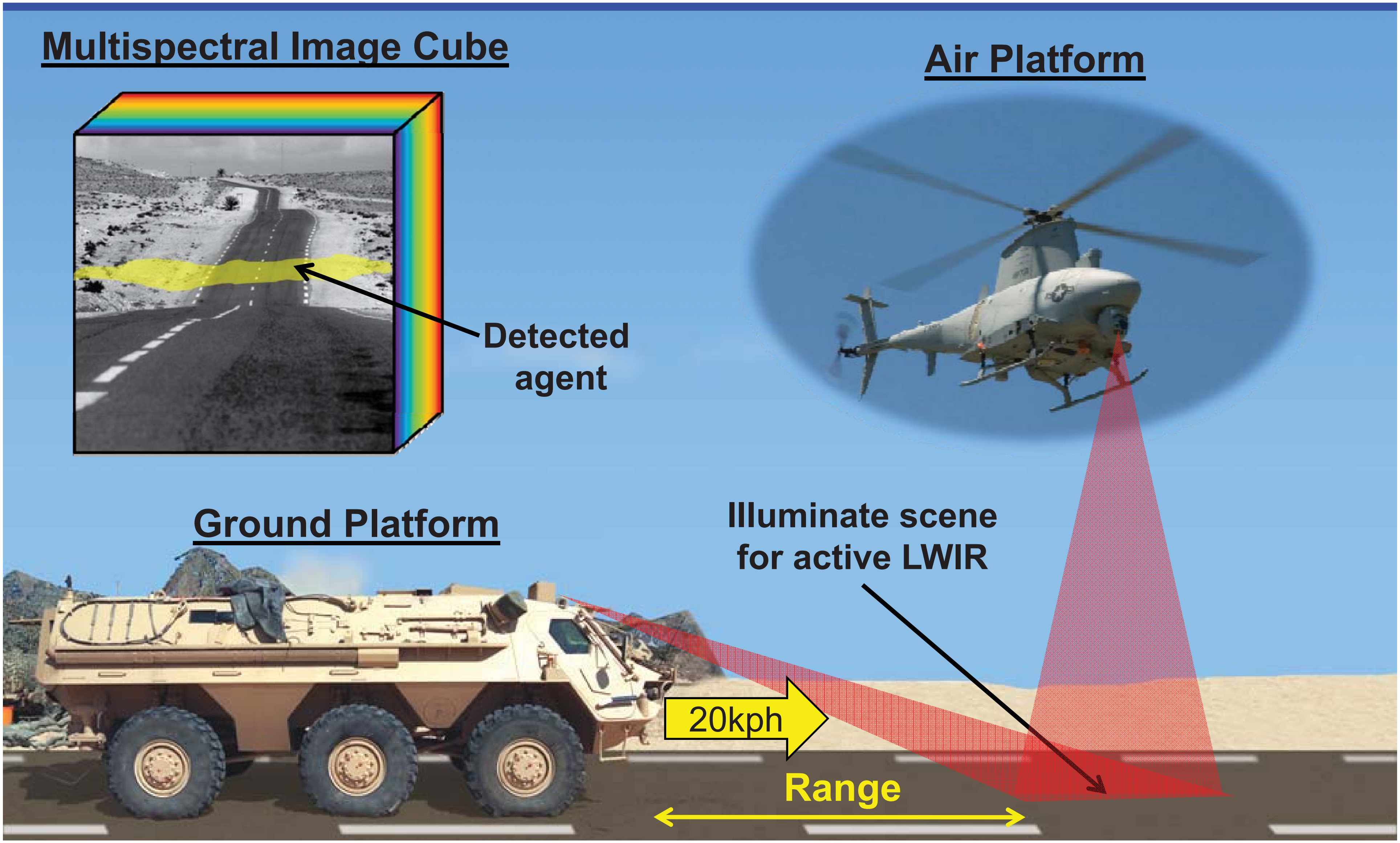
Assumes JCSD $\mathbf{p}_{\mathbf{sensor}}$ = 1

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

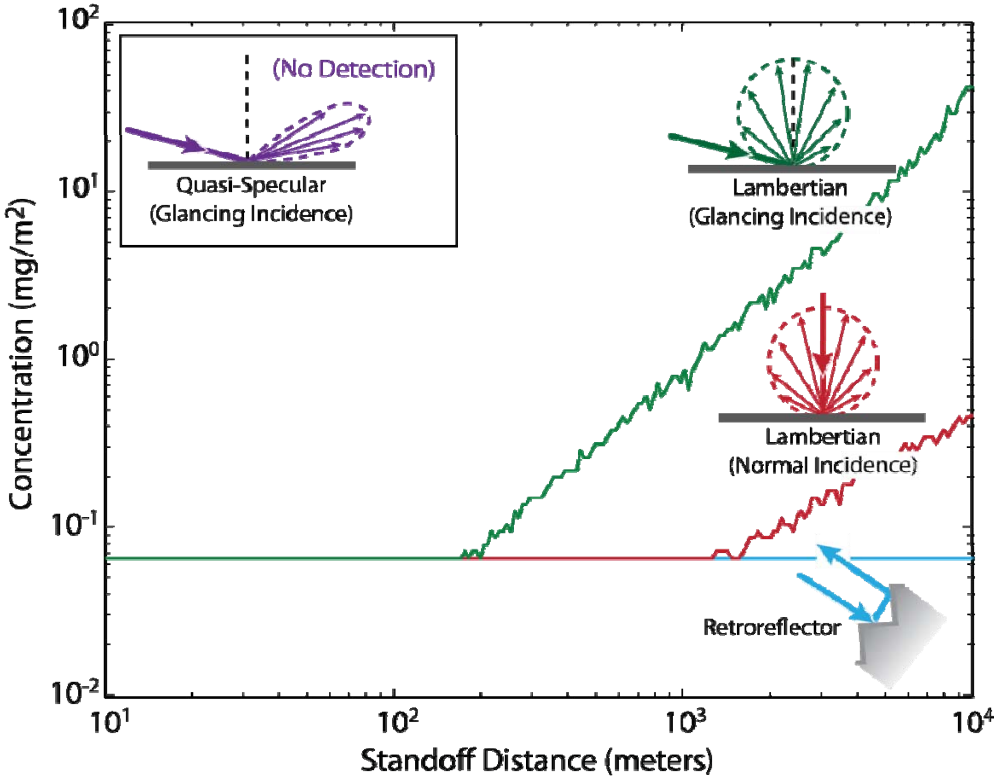
p_{drop} VX Sprayer	1 JCSD	3 JCSD
Maneuver droplet sizes	100%	100%
Fixed site droplet sizes	52.4%	89.2%

JCSD (as modeled) provides adequate warning for maneuver main force, however all scout vehicles expected to become contaminated

Maneuver: Active and Passive LWIR

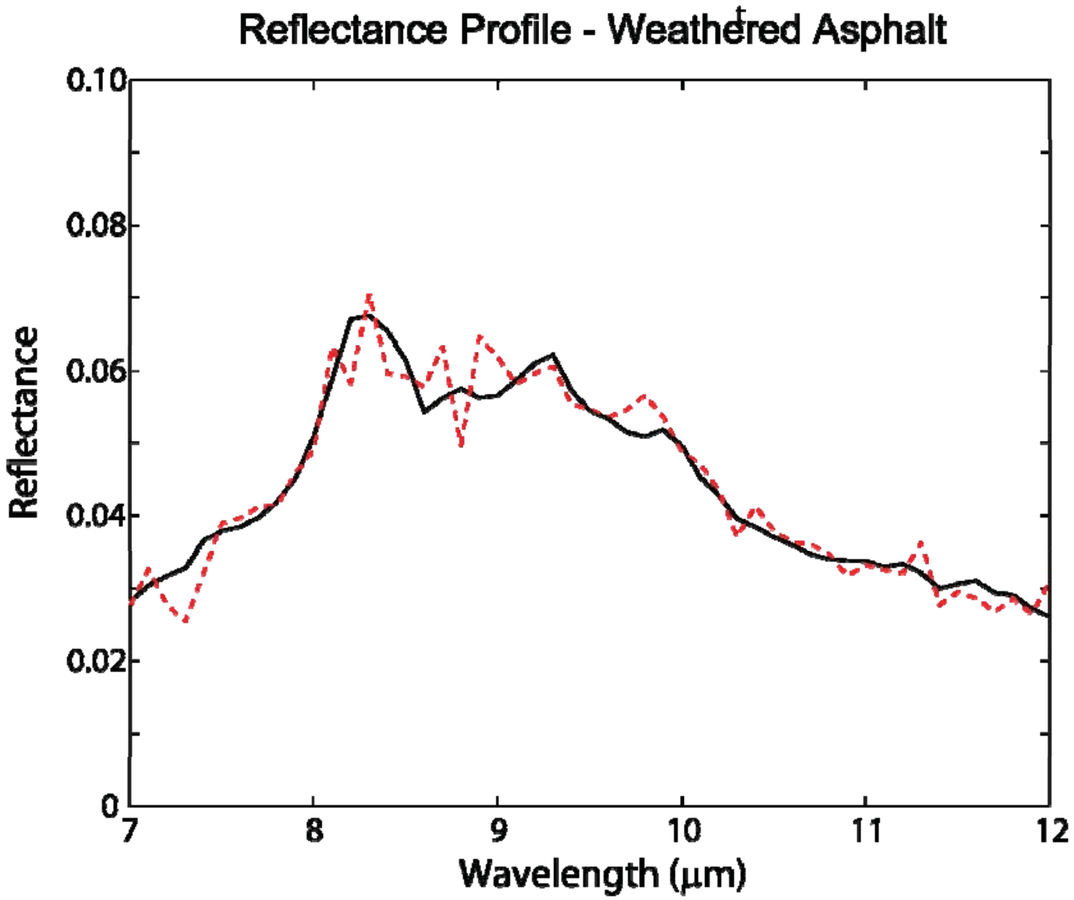


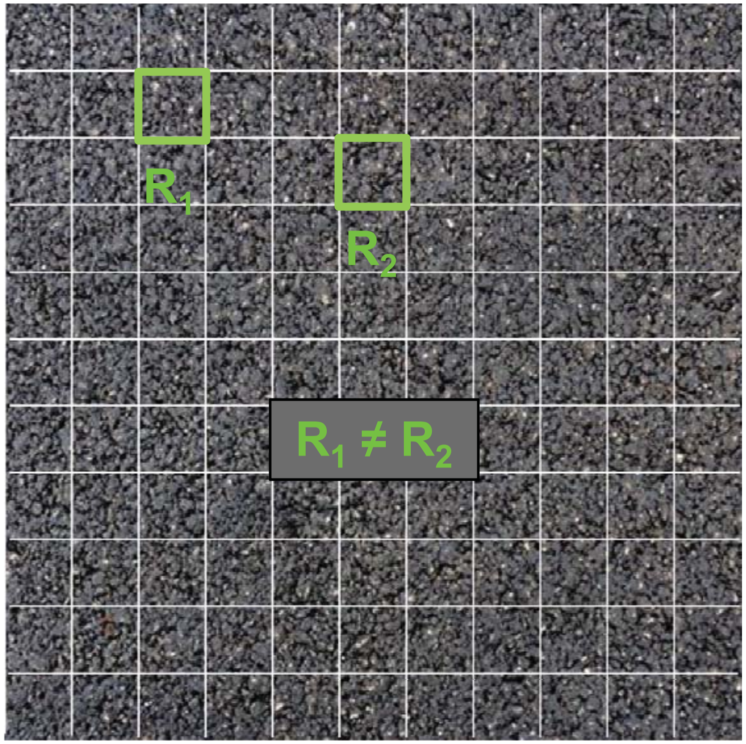
Maneuver:
Angular Dependence of Active LWIR


Detectable Concentration vs. Standoff Distance

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)

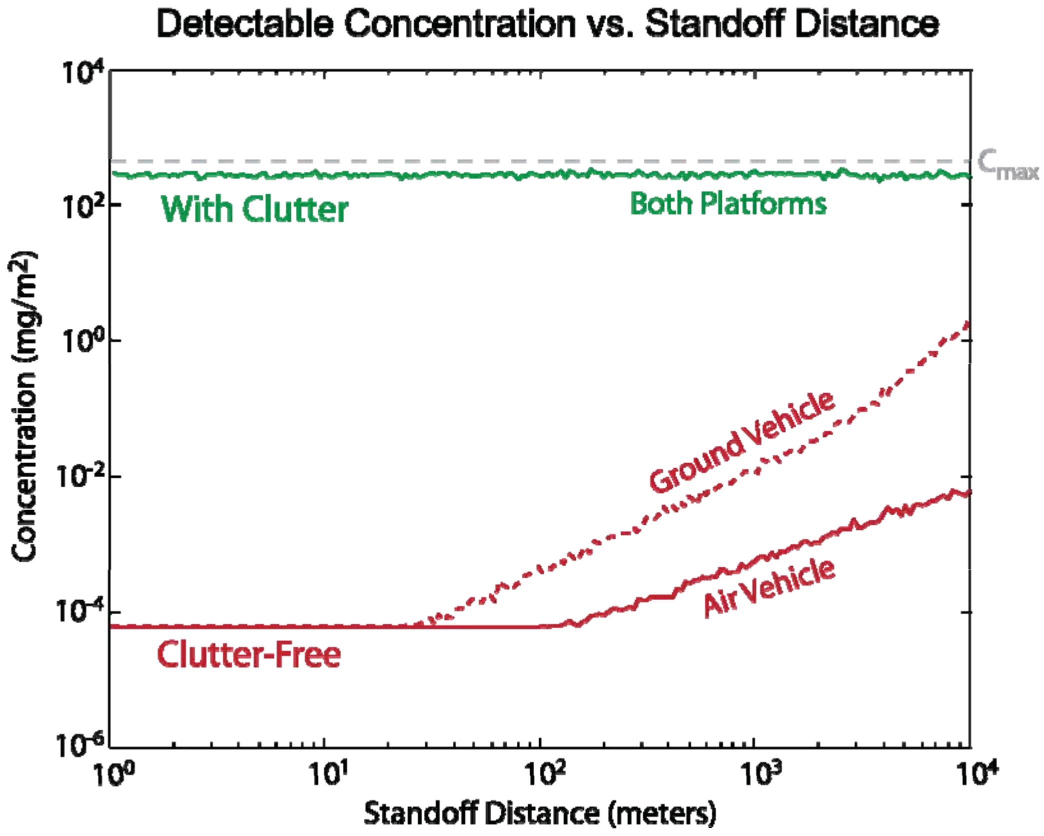
Maneuver:
Reflectance and Clutter


Reflectance Profile - Weathered Asphalt



Substrate reflectivity will vary from pixel to pixel, introducing noise we refer to as "**clutter**" during background subtraction

Maneuver:
Active LWIR Performance

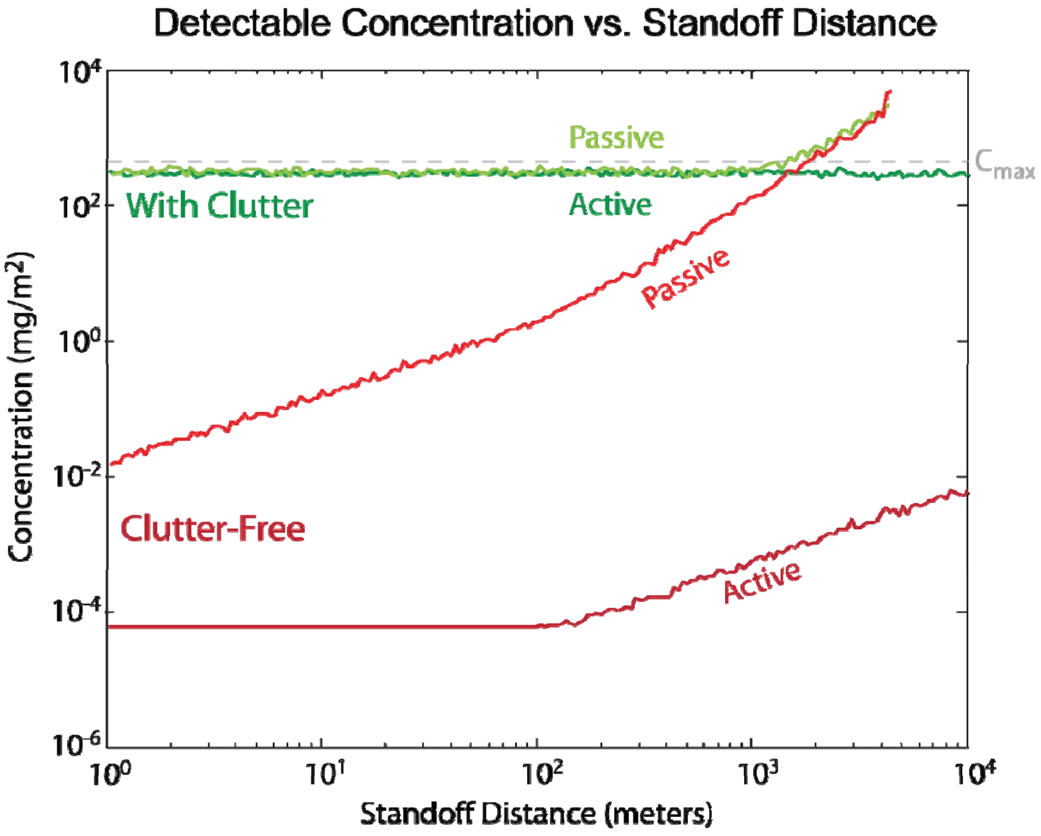


- In the absence of clutter, both platforms perform reasonably well
- With clutter, performance is clutter-limited and both platforms perform poorly
- Ability to detect only the highest concentration the vehicle is predicted to encounter, ground vehicle is likely to become contaminated

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

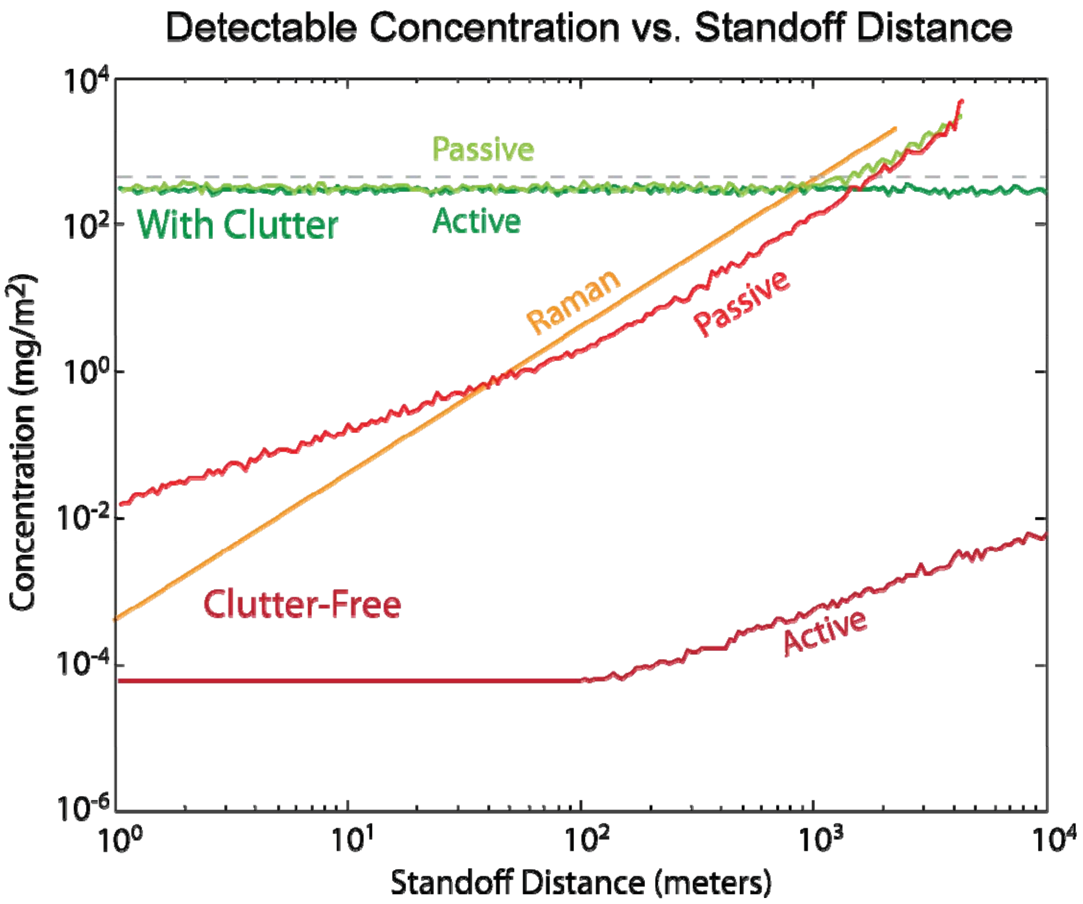
Detectable Concentration vs. Standoff Distance



- 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

Acknowledgements

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