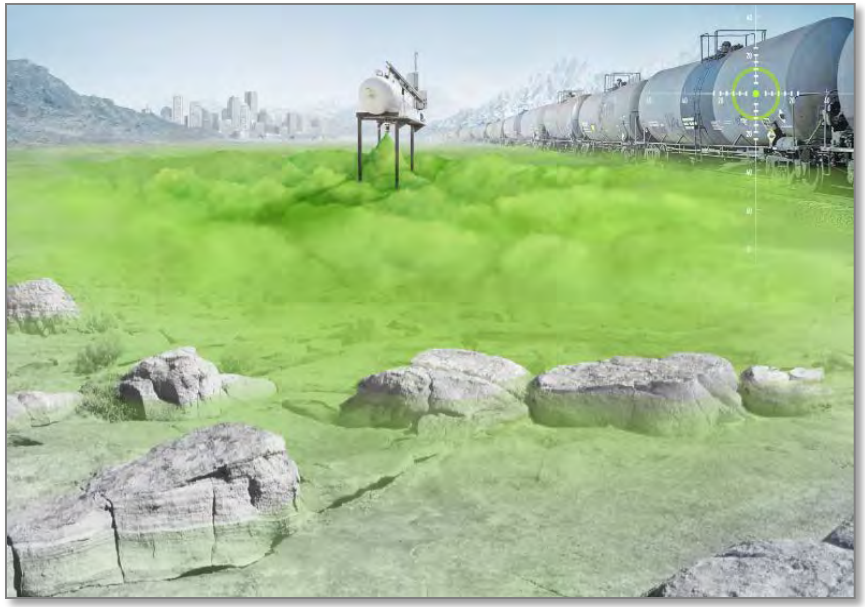
Project Jack Rabbit - Chlorine Chemical Reactions as a Loss Mechanism for Dense Plumes



Presented to:
Chlorine Institute
Technical Symposium
Houston, TX, April 8, 2013

Shannon Fox, Ph.D.
Senior Research Scientist, Project Manager
Chemical Security Analysis Center

Homeland Security
Science and Technology

Homeland Security
Science and Technology

Acknowledgements

- Air Force Research Laboratory (AFRL):
  Mike Henley, John Hearn, Howard Mayfield
- AFRL Contractors:
  Rich Weber, Jeff Eichler, and Bob Nichols
- U.S. Army Dugway Proving Ground, Meteorology Division:
  Donny Storwold, John White, John Pace and Team
- Funding:

Department of Homeland Security: Chemical Security Analysis Center, Transportation Security Administration

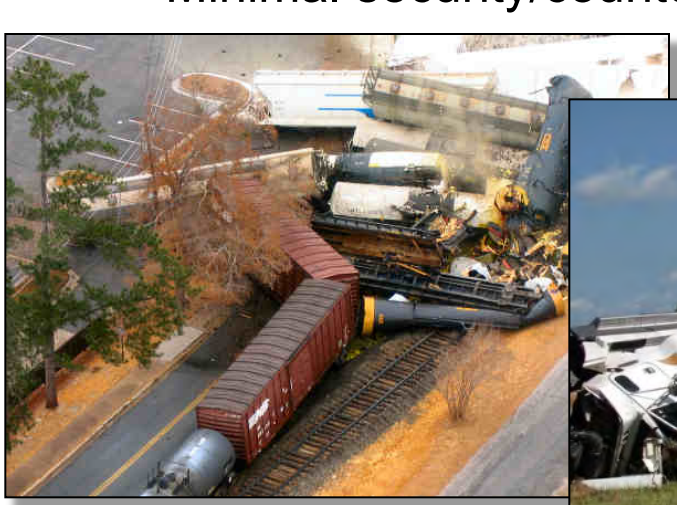
Defense Threat Reduction Agency

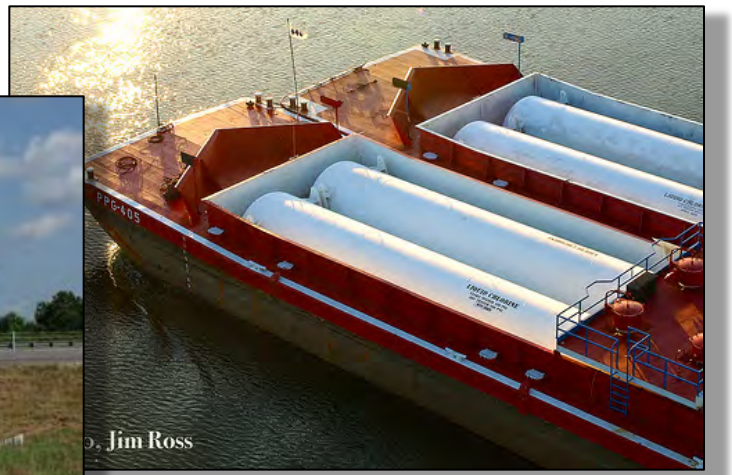
Industrial Partners: Association of American Railroads (AAR)
Center for Toxicology and Environmental Health (CTEH)

Homeland Security
Science and Technology

Transportation Risk

- Chlorine and Ammonia are essential to modern life
- *Hundreds of millions* of tons are transported every year by road, water, rail
- Chemicals are heavily trafficked in bulk through High-Threat Urban Areas
- Accidents are regular occurrences (major every 5-10 years)
- A chemical in transport is an potential target for terrorism:
  - No need for acquisition
  - High toxicity of many industrial chemicals creates the potential for mass casualties in large-scale releases
  - Built-in delivery system to the target (hijack or attack in place)
  - Minimal security/countermeasures available

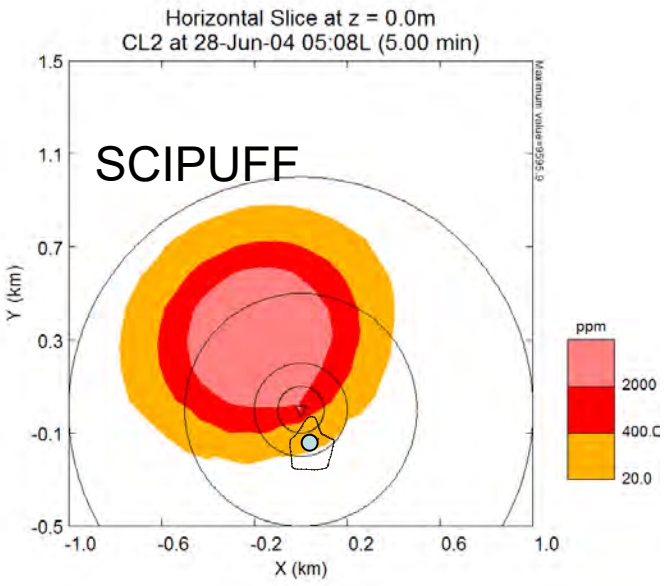


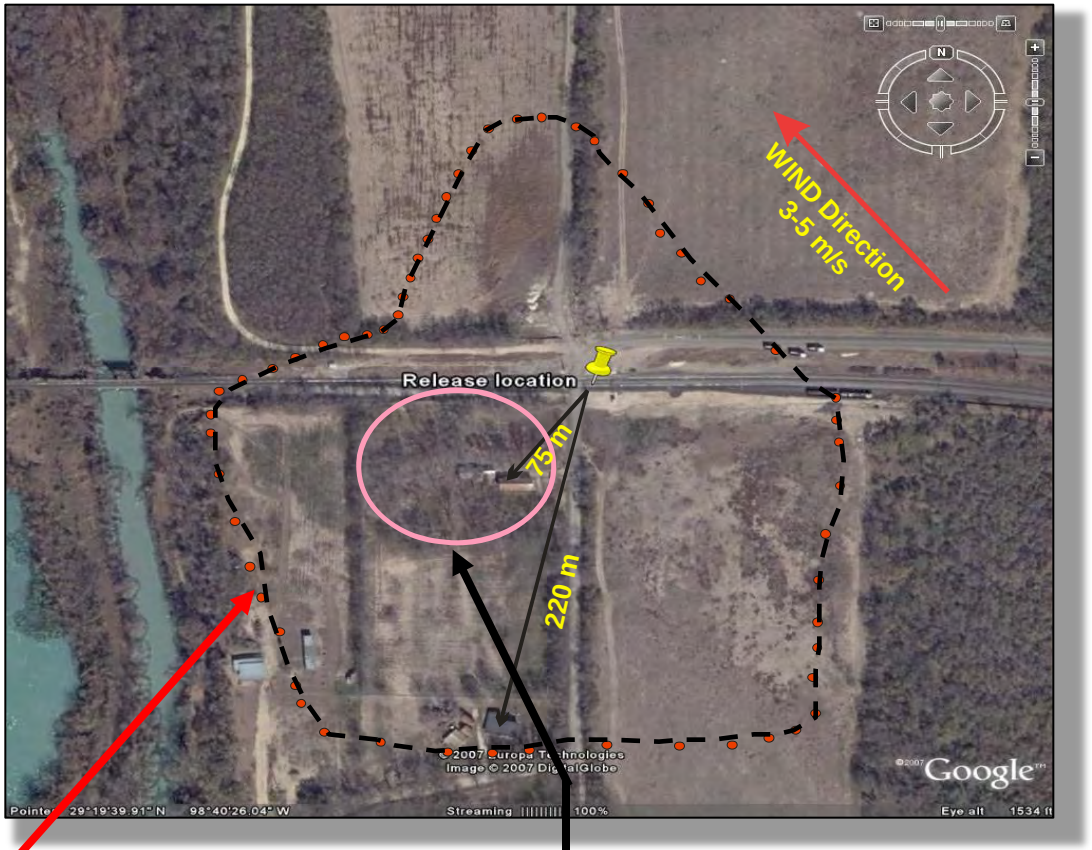


Homeland Security
Science and Technology

Chlorine Railcar Release – MacDona, TX

- Train collision in 2004
- 60 tons of chlorine released from rail car
- 3 killed, 43 hospitalized
- Models and observed impact do not match





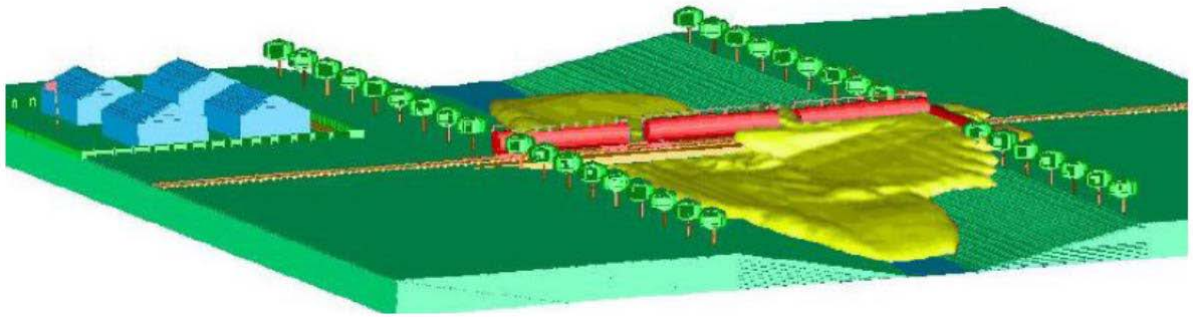
Limit of Vegetation Damage

14 Dead Animals and 3 Dead People inside of Ellipse only

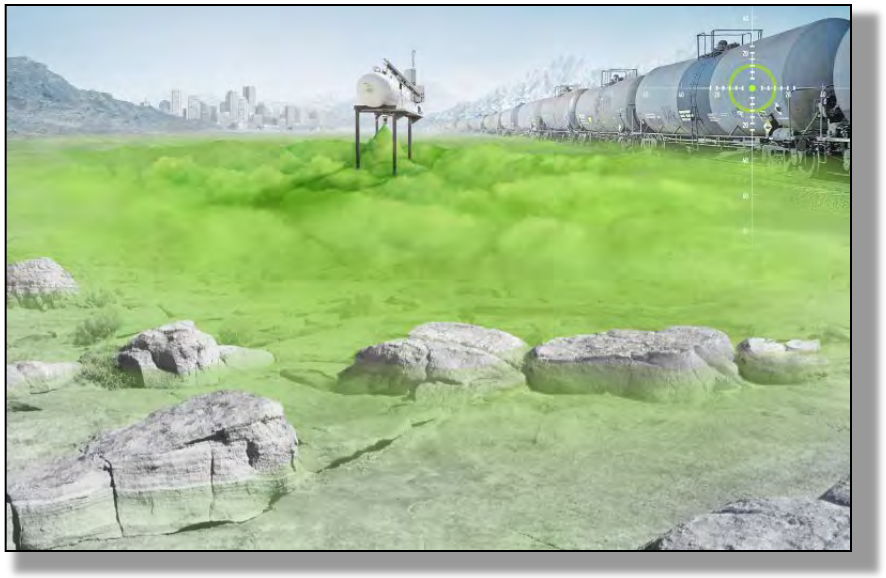
Homeland Security
Science and Technology

Problem Statement

- Problem: DHS and other agencies *must better understand behavior and consequences* of large-scale toxic inhalation hazard (TIH) chemical releases
  - Improve where modeling and predictions do not align with observations
  - ***Validated*** data and modeling for large-scale TIH releases (Cl_2, NH_3, SO_2, etc.)
  - Need improved understanding of dense-gas behavior, ***chemical reactivity***, toxicity, and source terms
  - Inform and emergency response and optimally define evacuation
- Solution:
  - Large-scale TIH field release experiments
  - Output: Knowledge products that are required for improved capabilities and efficiencies in planning, response and mitigation
    - Resiliency - better planning, emergency response
    - Vulnerability and impact reduction - Risk mitigation



Project Jack Rabbit - Overview



- CSAC funded to conduct field-releases of 2 tons of ammonia and chlorine in Spring 2010
- Releases configured to approximate release parameters and conditions hypothesized to exist at the large-scale
- Objectives:
  - Collect data on the source behavior of rapid, large-scale releases for the development of improved modeling source terms
  - Characterize the vapor/aerosol cloud movement
  - Evaluate chemical reactivity with soil as a loss mechanism for clouds
  - Compare ammonia and chlorine release behavior
  - Evaluate fielded instrumentation and develop and evaluate testing methodology for future additional and potentially larger-scale tests

Homeland Security
Science and Technology

Jack Rabbit Participants

Naval Surface Warfare Center - Dahlgren

- *Corrosive effects on military electronics*
- *On-site source modeling*

Air Force Research Lab Wright Patterson AFB

- *Compatibility testing with aircraft materials*
- *Long-term stress testing*

Safer Systems, Inc.

- *Deployed line-of-sight Infrared Boreal Laser*
- *Detection system*

Jack Rabbit

TSA
Sponsor

DHS-CSAC
Manager

Dugway
Performer

Signature Science, Inc.
- *Cloud Concentration*
- *Source Analysis*

Air Force Research Lab
- *Soil Core Sampling*
- *Reaction Analysis*

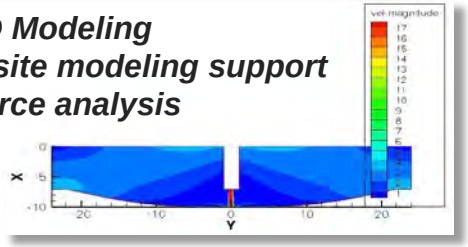
Co-sponsored by Association of American Railroads (AAR)

Center for Toxicology and Environmental Health

- *Instrumentation deployment – AreaRAE and MiniRAE detectors*
- *Fielding DHS S&T detectors*
- *Live plume mapping*

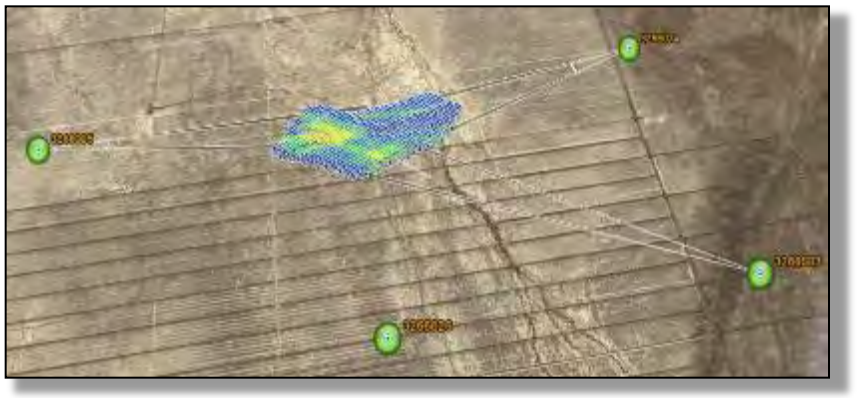
Forsvarets Forskningsinstitutt (FFI) The Norwegian Defense Research Establishment

- *CFD Modeling*
- *On-site modeling support*
- *Source analysis*



Jack Rabbit Trials

- Conducted during 4 weeks, Apr-May 2010 with Ammonia and Chlorine
- 1 ton (pilot) and 2 ton (record) releases
- Total of 10 successful trials (2 pilot, 8 record)
- Extensive array of instrumentation deployed empirically recording various aspects of the chemical releases
- High definition video documentation captured from multiple angles
- 3-Dimensional computerized cloud reconstructions
- Vast quantities of data generated
- Weather variation provided a range of different conditions



Homeland Security
Science and Technology

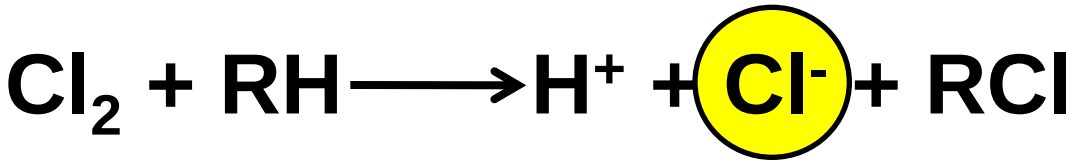
Jack Rabbit Release Videos

Trial	Date	Chemical	Amount
Pilot-NH_3	07-APR-10	Ammonia	1 Ton
Pilot-Cl_2	08-APR-10	Chlorine	1 Ton
01-RA	27-APR-10	Ammonia	2 Tons
02-RA	01-MAY-10	Ammonia	2 Tons
03-RC	03-MAY-10	Chlorine	2 Tons
04-RC	04-MAY-10	Chlorine	2 Tons
05-RC	05-MAY-10	Chlorine	2 Tons
06-RC	07-MAY-10	Chlorine	2 Tons
07-RA	20-MAY-10	Ammonia	2 Tons
08-RA	21-MAY-10	Ammonia	2 Tons

Homeland Security
Science and Technology

Background

- Attenuation mechanisms
  - Dispersion (physical)
  - Gas-phase chemistry (photolysis, reaction with atmospheric oxidants)
  - Heterogeneous deposition



$Cl_2 + H_2O \longleftrightarrow HCl + HOCl$

$HOCl + OH^- \longleftrightarrow H_2O + OCl^-$

$HOCl/OCl^- + \text{organics} \longrightarrow \text{loss}$

Photolytic: $\longleftrightarrow$

$Cl_2 + \text{light} \longrightarrow 2Cl\bullet$

$Cl\bullet + RH \longrightarrow HCl + R\bullet$

$R\bullet + Cl_2 \longrightarrow RCl + Cl\bullet$

Homeland Security
Science and Technology

Background

- The primary product is the chloride ion (Cl–), and the molar Cl– yield is equivalent to the Cl_2 loss with, the following three assumptions:

1. The pH is high enough so that HCl(g) does not evolve

2. Acid-catalyzed addition of Cl– to carbon–carbon double bonds is not significant

3. Direct addition of Cl_2 to carbon–carbon double bonds is insignificant.

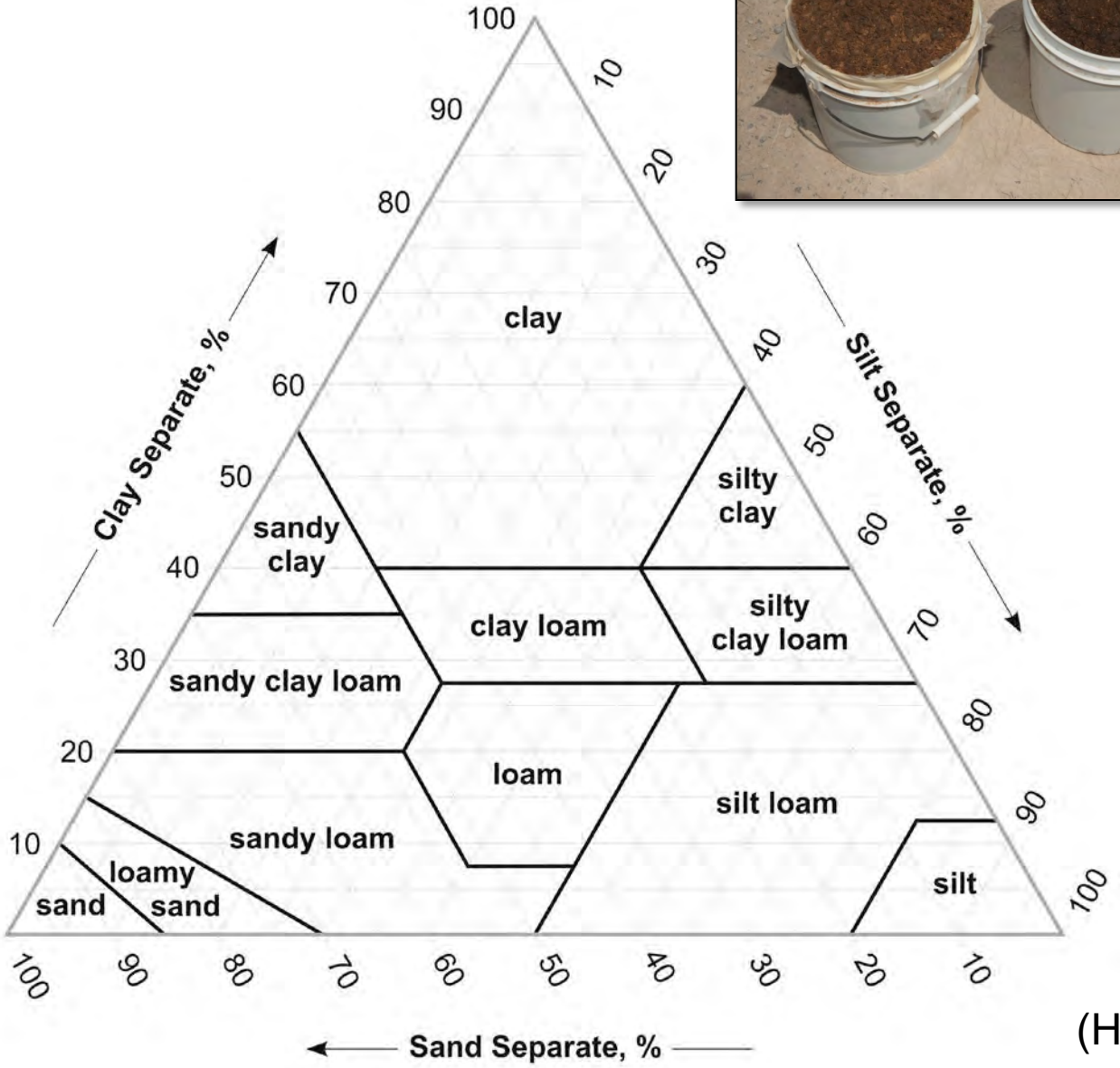
- Any contribution of these processes during Cl_2 deposition will not be accounted for by the Cl– measurements
- Therefore, Cl– provides ***a conservative marker*** for the total C_{l2} deposited.

$$Cl_2 + RH \longrightarrow H^+ + Cl^- + RCl$$

Homeland Security
Science and Technology

Samples

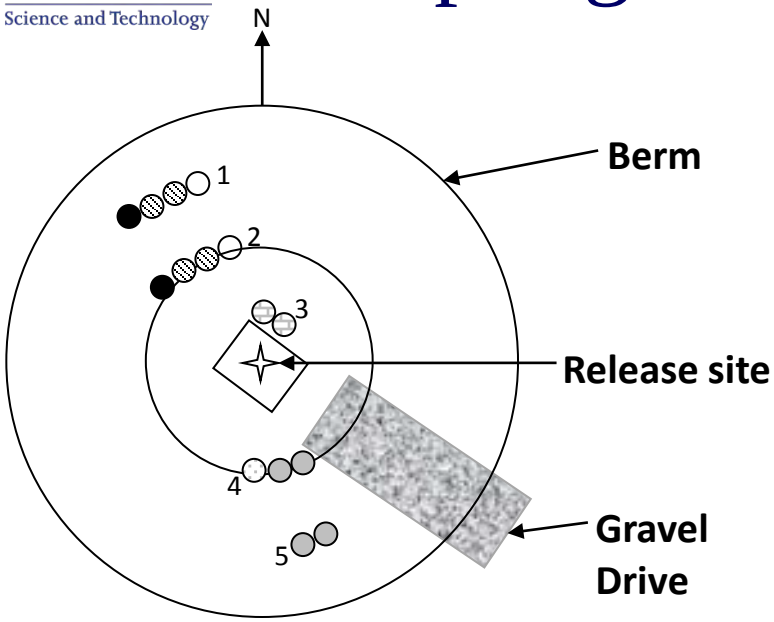
Dugway Clay



Sand
(Home Depot)

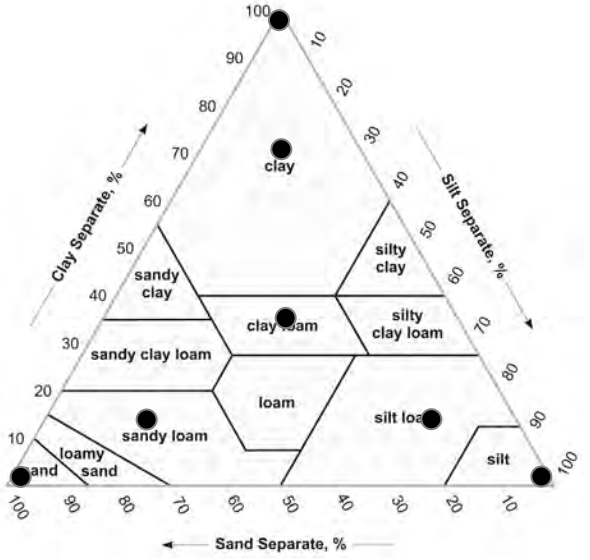
Top Soil
(Home Depot)

Sampling Strategy

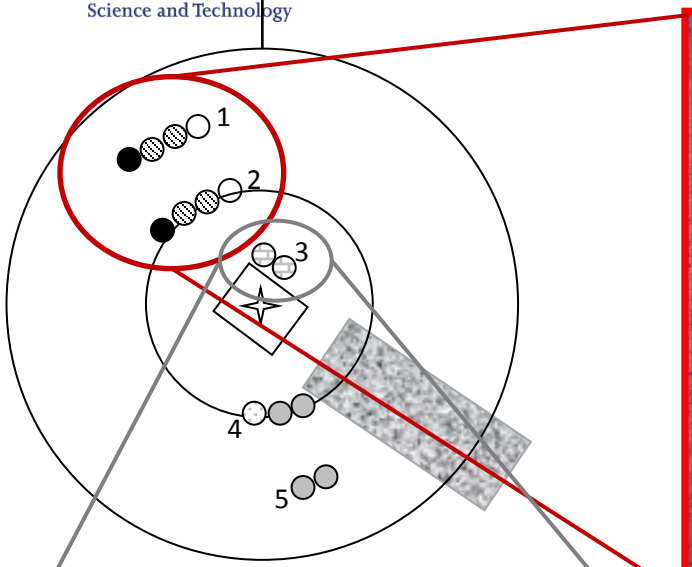


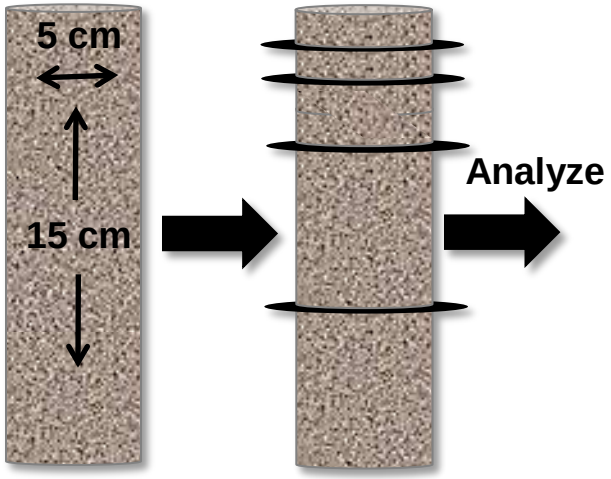
Site #	Distance	Height
1 & 5	15 m	1 m
2 & 4	10 m	0 m
3	2 – 3 m	0 m

Soil Number	Name	% Clay	% Sand	% Silt	Water
1	Sandy loam	15	70	15	No
2	Silt loam	15	15	70	No
3	Clay loam	33	33	33	No
4	Clay loam wet	33	33	33	Yes
5	Clay	70	15	15	No
6	Sand	0	100	0	No
7	Silt	0	0	100	No
8	Clay 100	100	0	0	No



Sampling Strategy



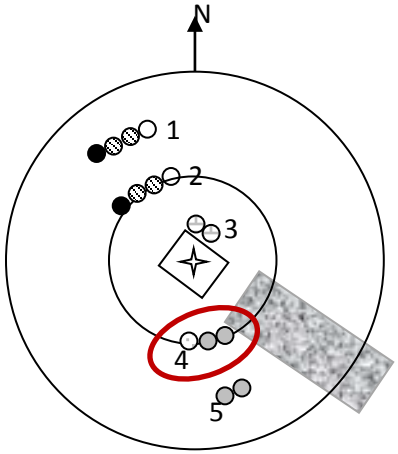


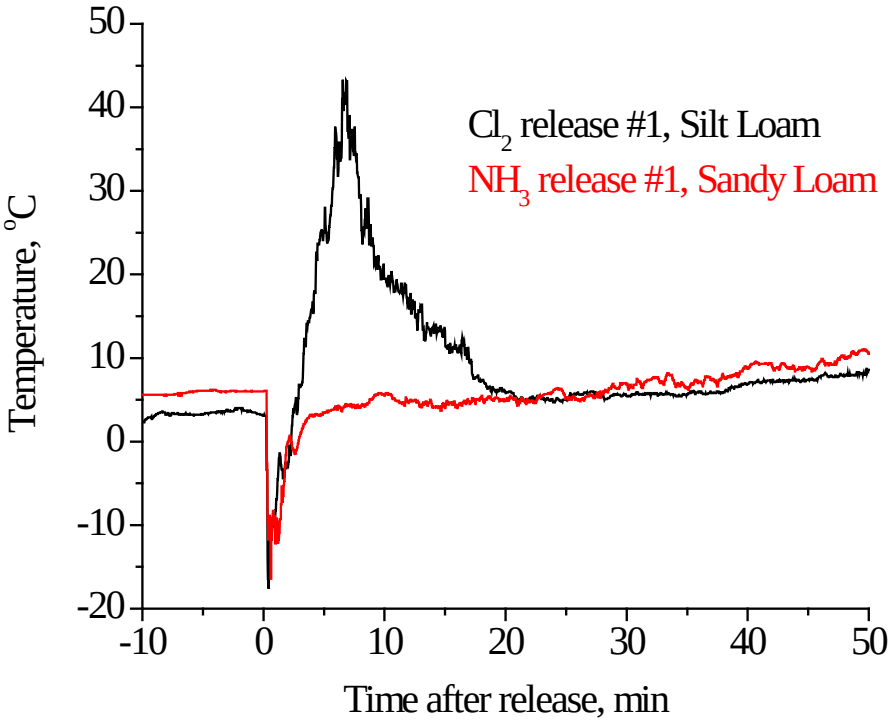
1. Ion chromatography of extract
2. Water mass fraction (gravimetric)
3. Total organic content (gravimetric)
4. Headspace analysis (GC-MS)

Cores Taken From Sample Buckets

Soil Temperature

- Thermocouples at and below ground measured temperature increase
- This is an indication that large reaction enthalpy is present



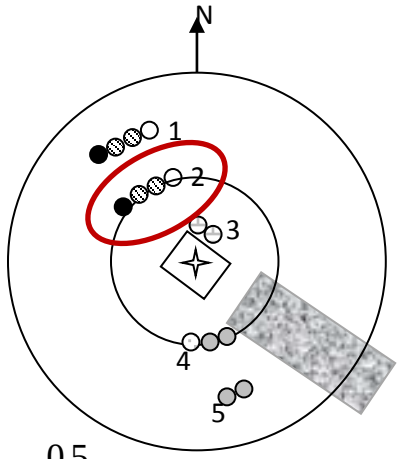


	$\Delta_{sol}H$
Cl_2	-19.75 kJ/mol*
NH_3	-30.5 kJ/mol**

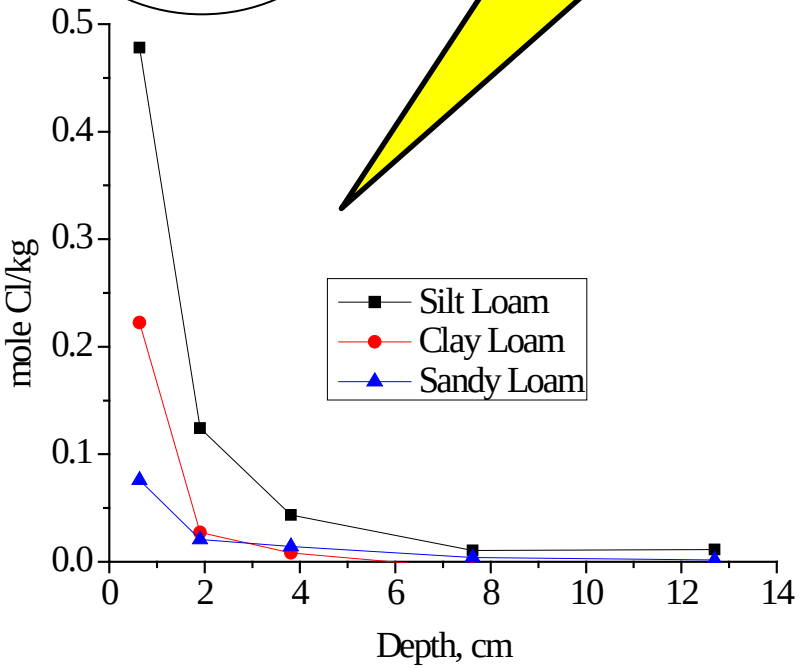
* M. Alkan (2005)
** CRC Handbook (1995)

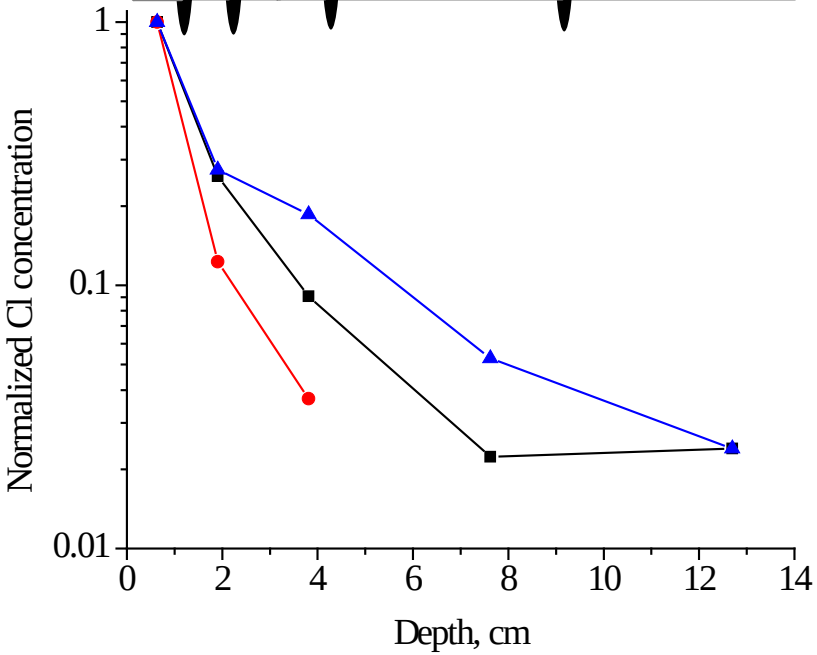
Homeland Security
Science and Technology

Cl_2 Release #1

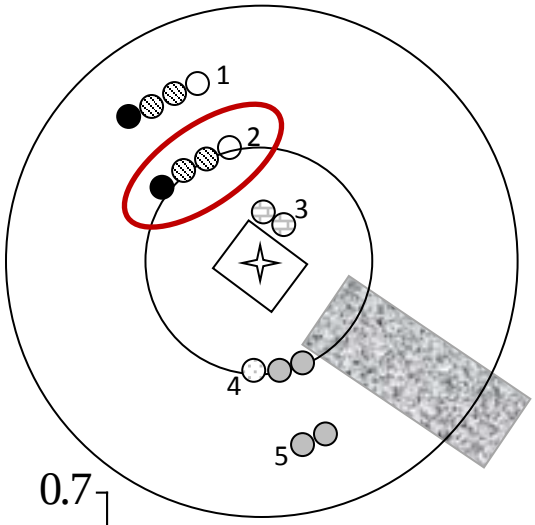


Silt Loam > Clay Loam > Sandy Loam



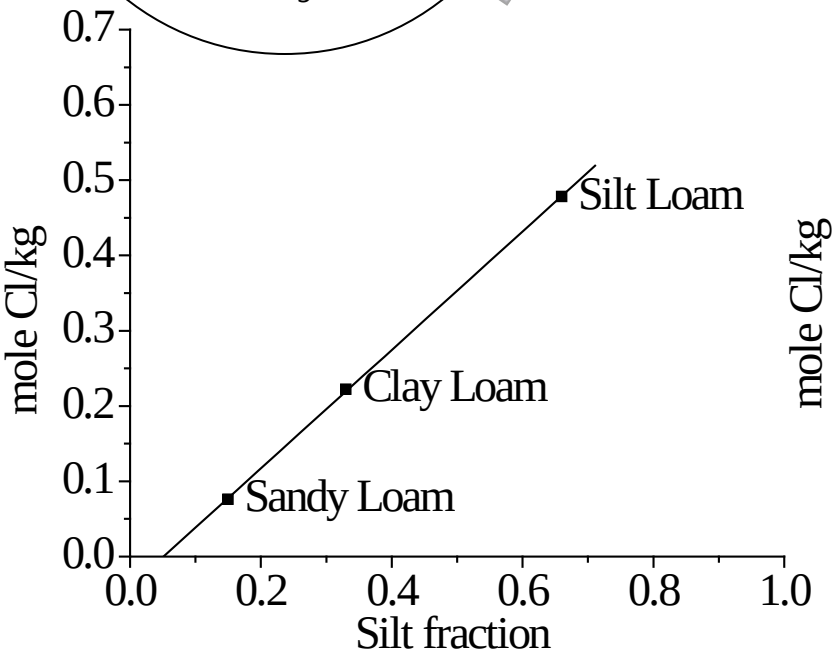


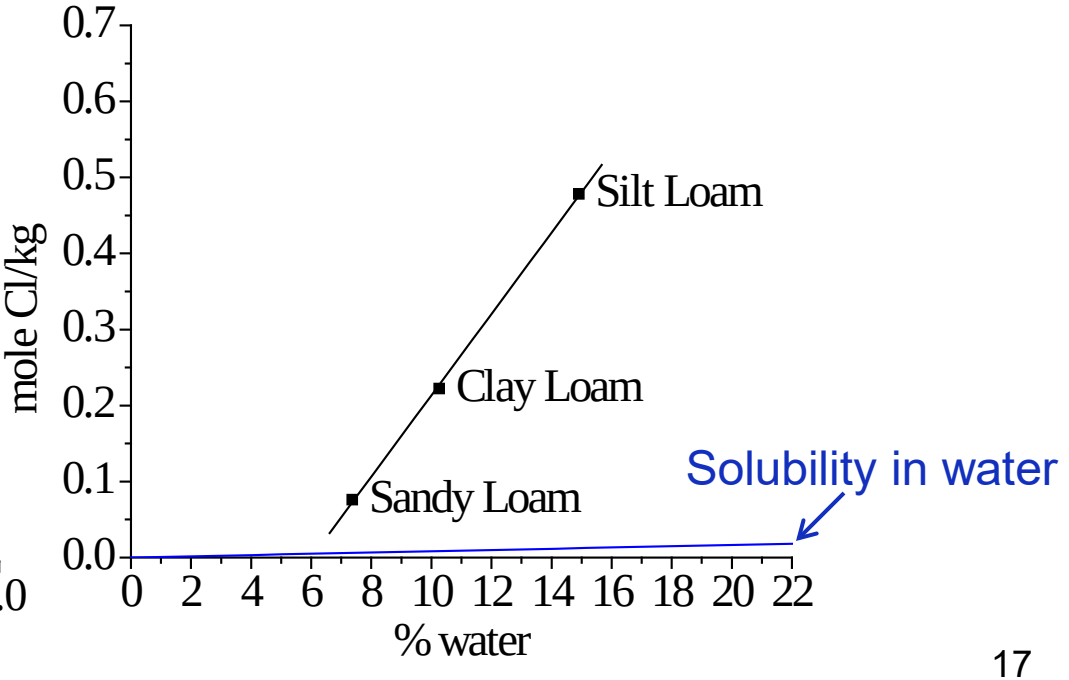
Dependence on Soil Composition



Cl_2 release #1
Samples at site 2 (10 m NW)
Top fraction (0.5 in)

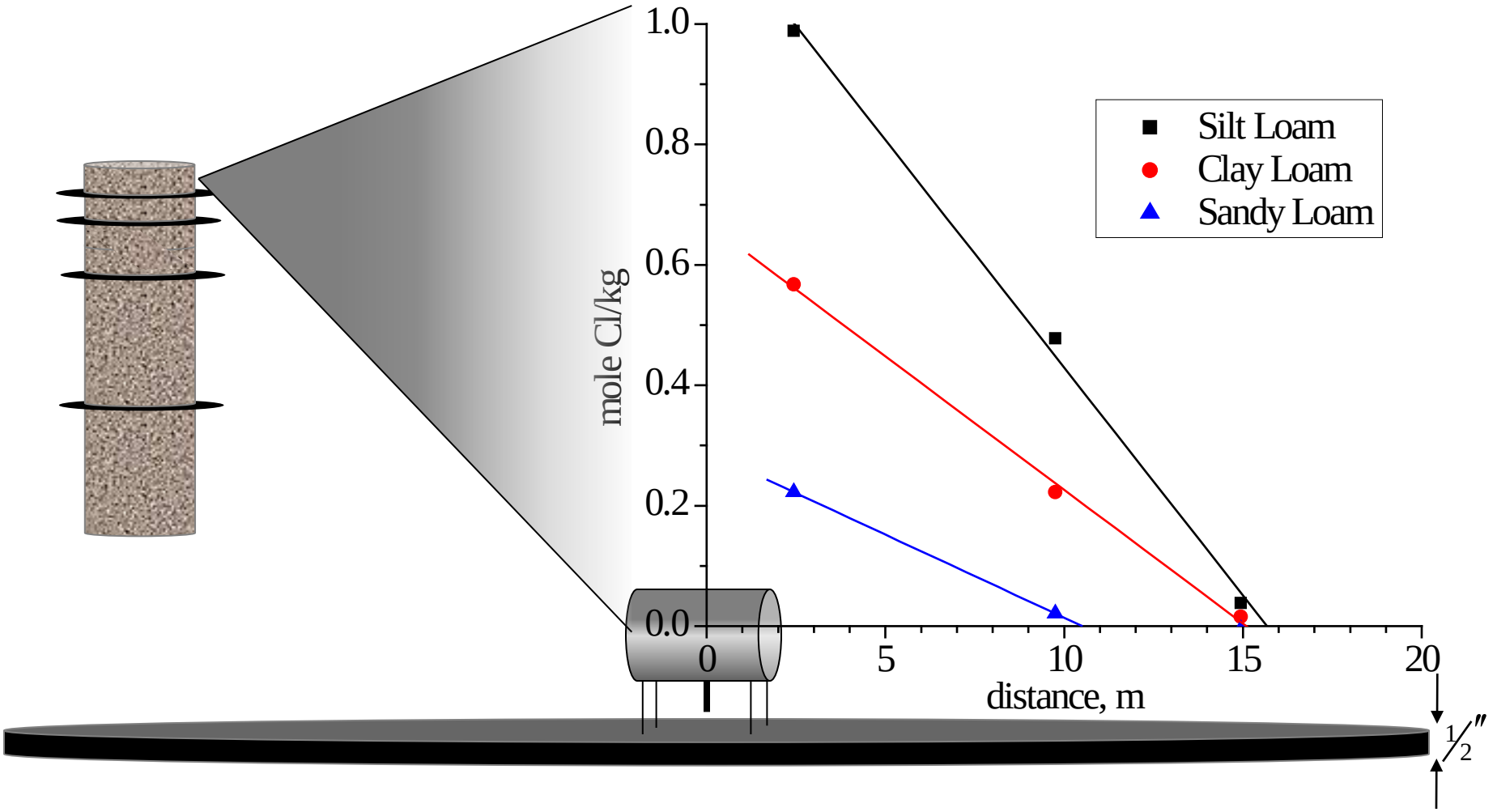
$$Cl_2 + H_2O \longleftrightarrow HCl + HOCl$$
$$HOCl + OH^- \longleftrightarrow H_2O + OCl^-$$
$$HOCl/OCl^- + \text{organics} \longrightarrow \text{loss}$$



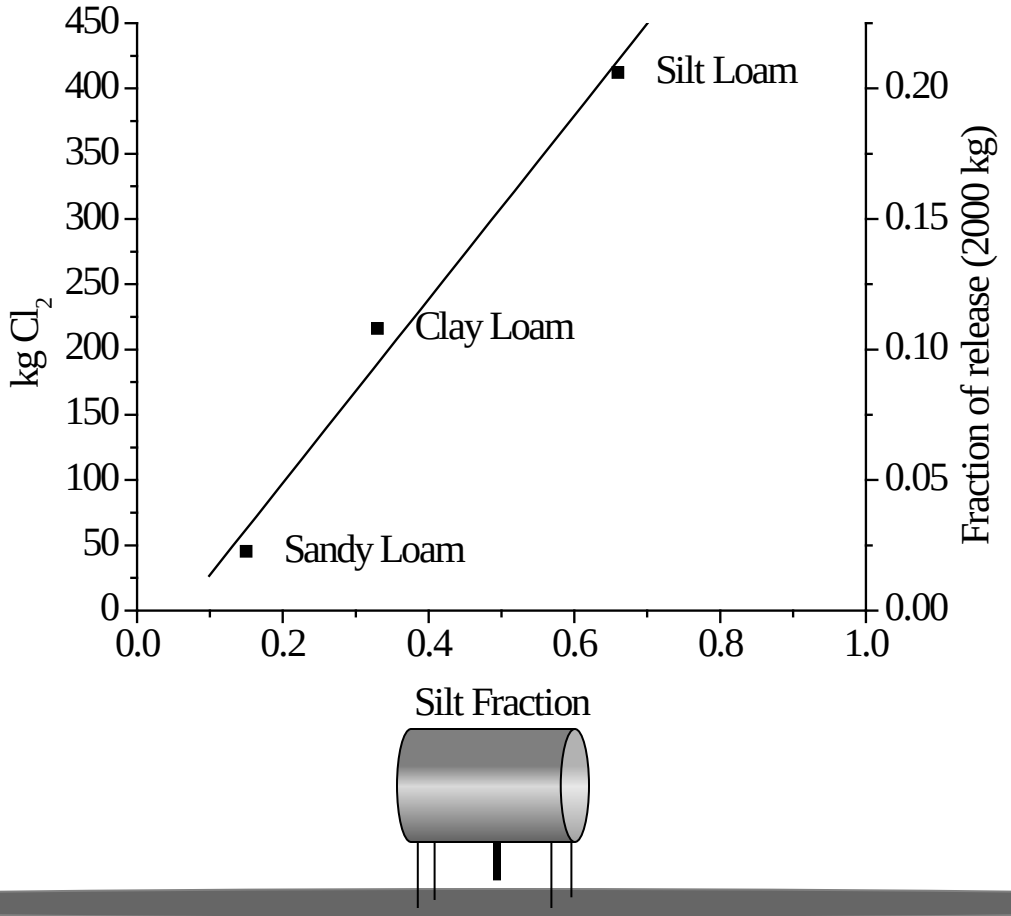


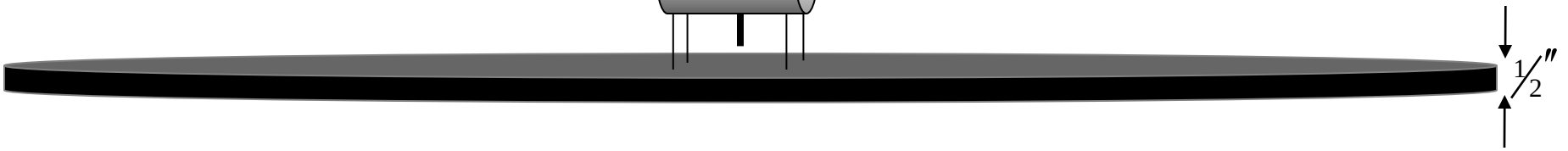
Homeland Security
Science and Technology

Impact of Deposition



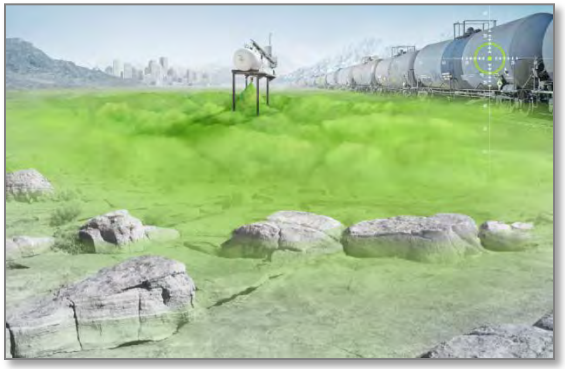
Impact of Deposition





Homeland Security
Science and Technology

Summary



- For the determination of deposition with soil as a loss term for chlorine:
  - [Cl–] results from the top 1.3 cm vertical fractions were used
  - Analyses involved trials with low-wind (≤1.6 m/s) conditions.
  - **The analysis revealed up to 50% of a 1814-kg chlorine release could be removed within 20 m from the release point for soil with high organic matter (43%) and/or water content (29%).**
- Enormous implications for modeling, planning, emergency response, and mitigation
- Reaching out to network of model developers to provide data for incorporating deposition removal terms for chorine
- Additional data and findings from this study can be found in our new publication in Journal of Hazardous Materials

Homeland Security
Science and Technology

Publication

- This work has recently been published in the latest issue of the Journal of Hazardous Materials (JHM)

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

ELSEVIER journal homepage: www.elsevier.com/locate/jhazmat

Deposition of Cl_2 on soils during outdoor releases

John D. Hearn[a,*], Richard Weber[b,1], Robert Nichols[c], Michael V. Henley[a], Shannon Fox[d]

[a] Air Force Research Laboratory, Airbase Technologies Division, 139 Barnes Drive, Suite 2, Tyndall Air Force Base, FL 32403-5323, United States
[b] Applied Research Associates, 139 Barnes Drive, Suite 2, Tyndall Air Force Base, FL 32403-5323, United States
[c] Universal Technology Corporation, 139 Barnes Drive, Suite 2, Tyndall Air Force Base, FL 32403-5323, United States
[d] Chemical Security Analysis Center, Department of Homeland Security, Aberdeen Proving Ground, MD, United States

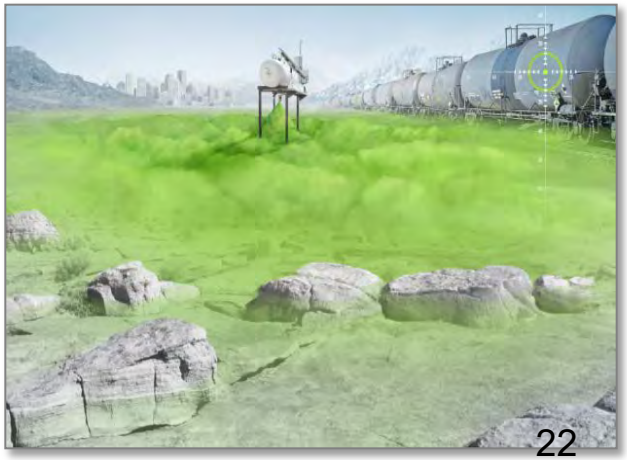
- *Journal of Hazardous Materials* 252– 253 (2013) 107– 114.
- Details and additional aspects of this study may be found in this article

Homeland Security
Science and Technology

Jack Rabbit II – New Program

We will conduct a new series of open-air chlorine release trials in a multi-agency effort, building upon the work performed in Jack Rabbit I

- FY14 – 17 project approved by DHS S&T HSARPA for funding
- DHS CSAC will lead – seeking multi-agency co-investment and participation
- Larger volume chlorine field releases from 5 to 20 tons
  - Continuing evolution of higher quantity releases – scaling is non-linear
  - 20 tons represents 100% of tanker truck transport volume, and a large fraction of a railcar release
- Largest & most comprehensive source term study
- Longest down-wind dispersion study of its kind
- Quantitative determination of chlorine removal via reactivity with soil, atmosphere, vegetation, metals, and other surfaces
- Urban Impact Assessment–Mock Urban Test Bed



Homeland Security
Science and Technology

Jack Rabbit II Technical Approach

Jack Rabbit I	Identified Gaps	Jack Rabbit II Solution
1 and 2-ton releases	Larger-scale releases needed – evidence effects do not scale linearly with amount	**5, 10, 20-ton releases**
Flat desert and a 50 meter-wide terrain depression	Effect of terrain, obstacles, and buildings, on cloud movement and behavior	**Mock urban test-bed, engineered with terrain and building features**
Source term data for mass-flux and impingement	Source-term mass-balance needed for dense gases – currently *not experimentally validated beyond 2-tons*	**Comprehensive source term data: two-phase flow, pooling, rainout, retention, and off-gassing**
0.5-km downwind dispersion measurements (ground level)	Validation of dispersion models and ER needed beyond 0.5 km	**11-km downwind dispersion data, with vertical sampling for 3-D mass-balance**
Discovery of violent Rapid Phase Transition (RPT) eruptions	Previously unknown phenomenon and hazard – needs characterization for ER safety	**Comprehensive experimental characterization of RPT phenomenology**
Soil chemical reactivity experiments	TIHs reactions can remove a substantial portion of clouds – magnitude of effects currently not considered in any model	**Laboratory and field experiments with soil, vegetation, rural/urban surfaces**
Field testing of LACIS and ARFCAM detectors	Detectors, equipment, and PPE needs testing and validation with realistic exposure profiles and concentrations	**Numerous devices/resources tested. Co-located deployment for real-time exposure profile**
Limited electronics and materials exposure testing	Comprehensive exposure impact assessments needed for electronics, materials, buildings, and infrastructure	**Total urban infrastructure impact assessment**

Partnership Opportunities

- Seeking partnerships with key stakeholders
- Several organizations have already communicated financially support or participate in Jack Rabbit II
- Potential collaborative contributions include:
  - Direct investment of funding support
  - Contribution of key personnel
  - Sponsoring of targeted experiments
  - Fielding and operating instrumentation with mutual data-sharing
  - Conducting or funding critical studies from the resulting data
- This approach was successfully demonstrated in Jack Rabbit I, greatly multiplying the impact and value of the test
- Partnership with the Chlor-Alkali industry will be coordinated through our new CRADA with the Chlorine Institute
- To discuss support or participation opportunities contact:

Dr. Shannon Fox, DHS CSAC
Shannon.Fox@st.dhs.gov
410-417-0906

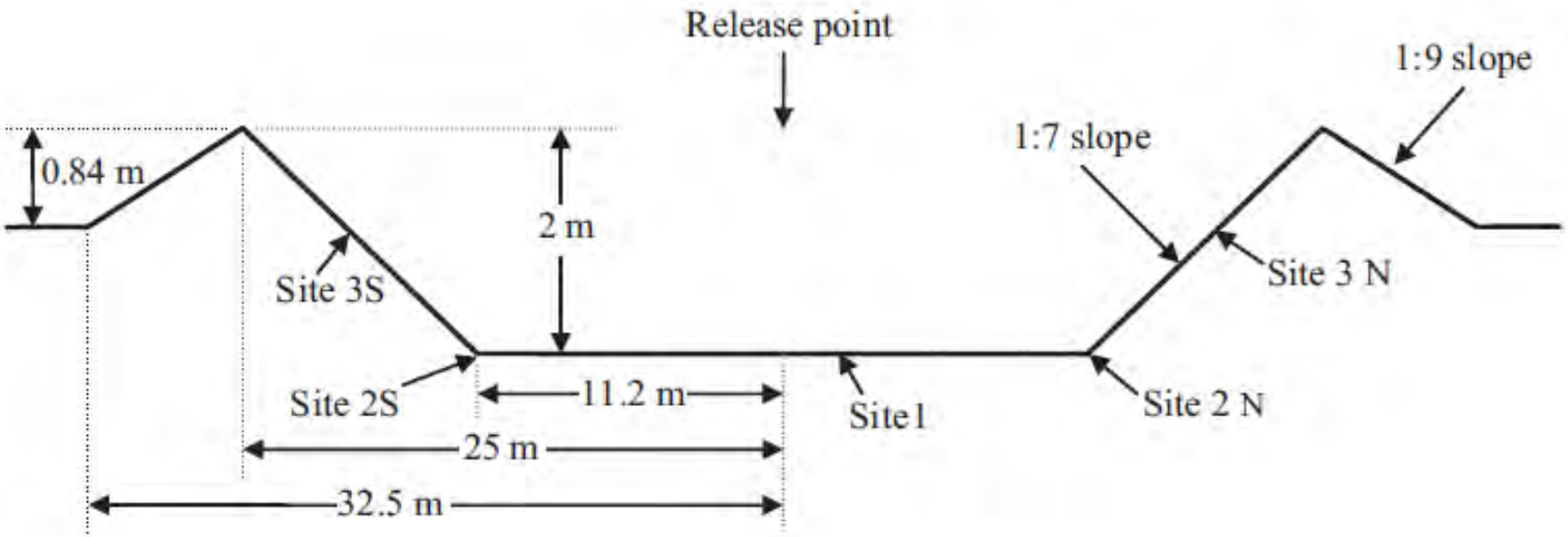
Homeland Security
Science and Technology

Questions

Homeland Security

Homeland Security
Science and Technology

Release Site Details



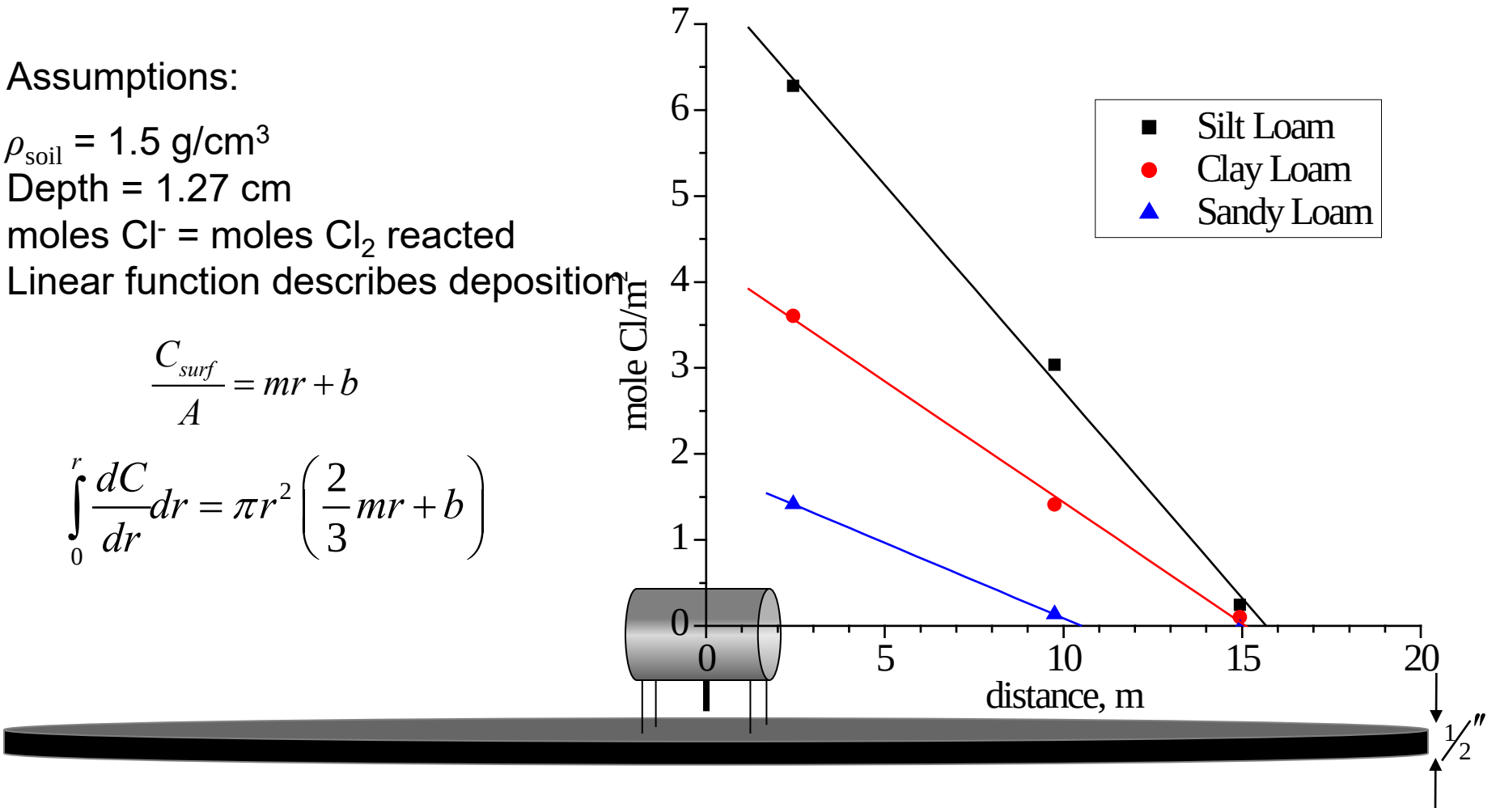
Impact of Deposition - Assumptions

Assumptions:

ρ_{soil} = 1.5 g/cm^3
Depth = 1.27 cm
moles Cl^- = moles Cl_2 reacted
Linear function describes deposition

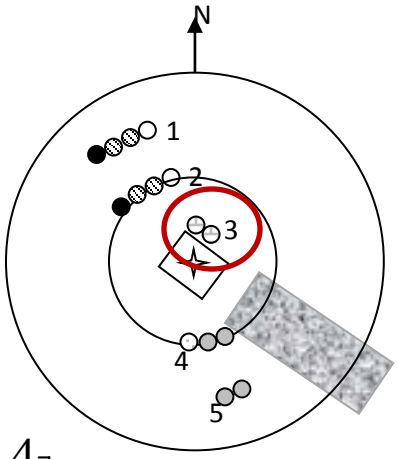
$$\frac{C_{surf}}{A} = mr + b$$

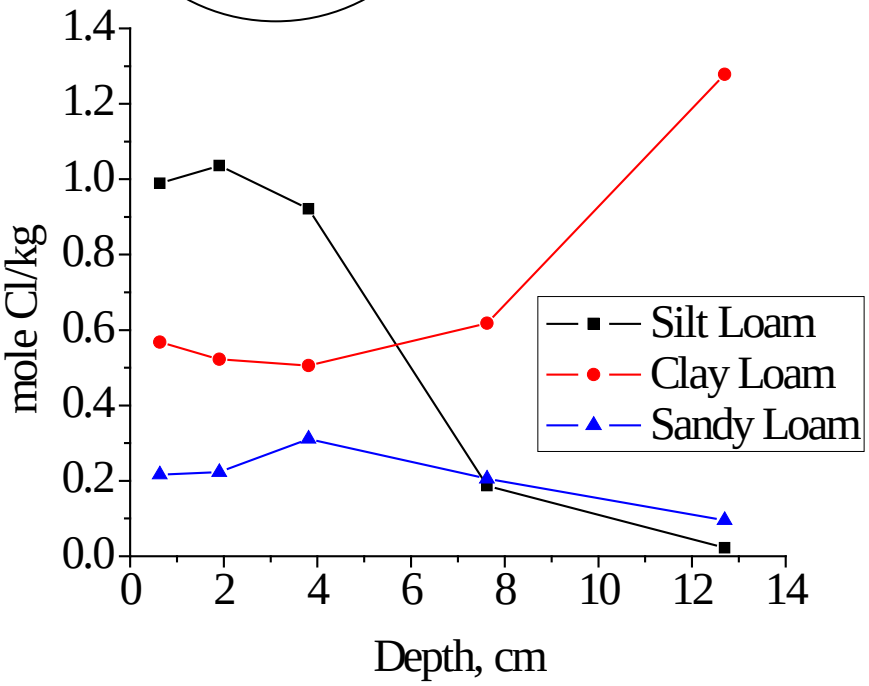
$$\int_0^r \frac{dC}{dr} dr = \pi r^2 \left(\frac{2}{3} mr + b \right)$$



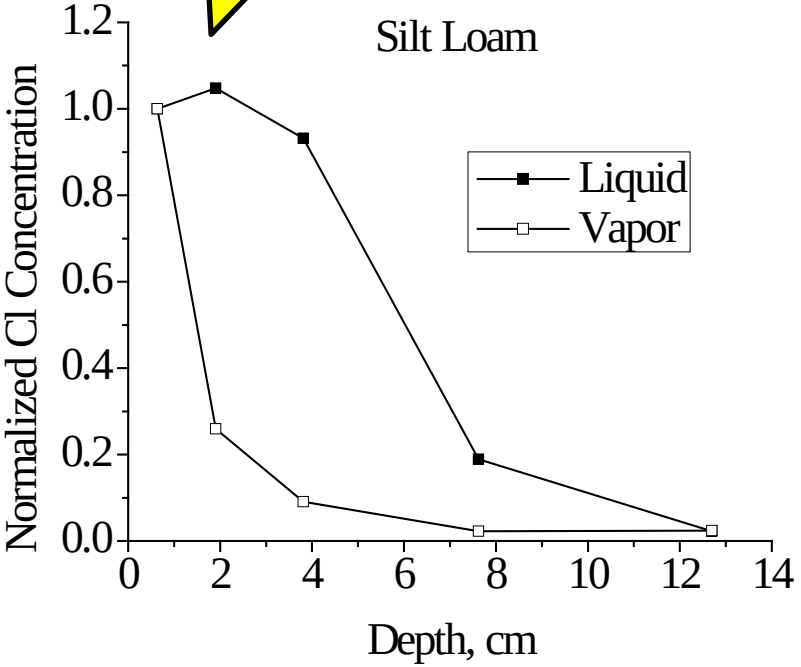
Homeland Security
Science and Technology

Cl_2 Release #1



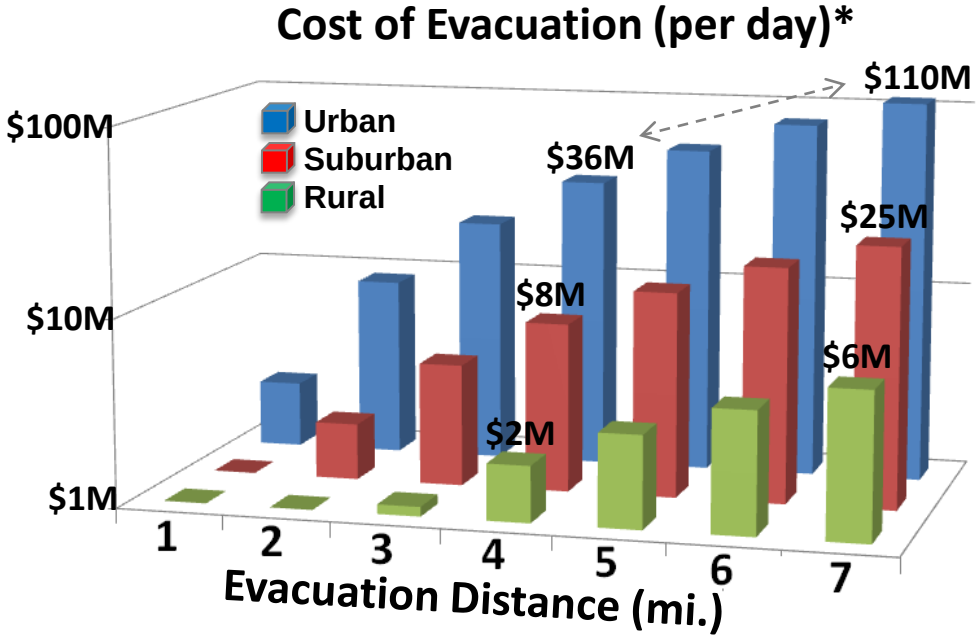


Deeper penetration of liquid



ROI Example – Evacuation

- Exponential increase in evacuation cost with longer distances
- Smaller, more accurately-determined evacuation distances result in large ROI.
- New evacuation distance projected to be 4 miles or less.



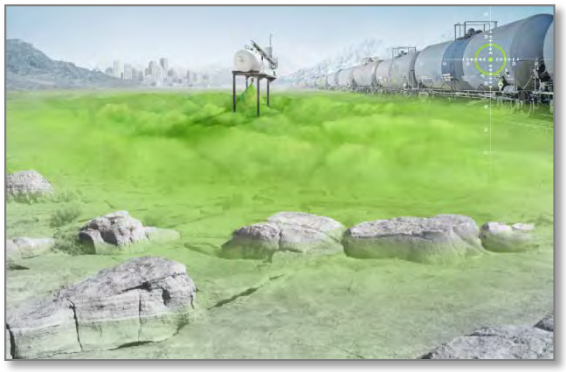
- ROI for reducing the evacuation distance from 7 to 4 miles reflects the savings ***per day.***
- Historical large-scale TIH evacuations have generally lasted 7-10 days.

	As-Is (7+ mi.)	To-Be (4 mi.)	**ROI (per day)**
Urban	$ 110M	$ 36M	**$ 74M**
Suburban	$ 25M	$ 8M	**$ 17M**
Rural	$ 6M	$ 2M	**$ 4M**

* U.S. DOT PHMSA, 2004, "Regulatory Flexibility Analysis - Hazardous Materials: Enhancing Rail Transportation Safety and Security for Hazardous Materials Shipments", PHMSA-RSPA-2004-18730.

Homeland Security
Science and Technology

JR II Summary

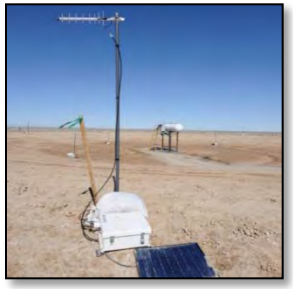


- **Need:**
  - Chlorine and TIHs are long-term, higher-frequency risks:
    - Large-scale accidents recurrent every 5-10 years
    - Documented and continuing threat of intentional release
  - Large-scale releases are poorly understood and characterized
  - Modeling capability is *must be improved* for large-scale Cl_2 and TIH releases
- **Multi-agency Partnerships**
  - Jack Rabbit I & II have broad interagency and private sector support
    - Several organizations plan co-investment into Jack Rabbit II
    - Many additional organizations have agreed to provide Letters of Support
- **Capabilities:**
  - Improved and validated source terms, AT&D modeling.
  - Unique and improved training capabilities – informed procedures and safety for responders
  - Novel mitigation measures evaluated and validated (chemical removal, trapping)
  - Improved shelter-in-place from building infiltration and urban impact characterization
- **Efficiencies:**
  - More efficient, focused, and informed emergency response will save money and lives
  - Improved efficiency of resource allocation (medical mitigation, response assets)
  - Realistic and optimized guidance improves evacuation efficiency

Jack Rabbit Findings

- Rapid Phase Transition (RPT) eruptions present a previously *unknown hazard* & are more likely with impingement
- Low winds and stable atmosphere results in cloud persistence
- Cold, dense gas is held up near release site and collects in low-lying areas

- Project Jack Rabbit was a project with limited-funding and scope which identified critical gaps requiring further experimentation and study.
- Stakeholders and partners in government, industry, and academia uniformly have communicated the need for ***definitive large-scale testing***



https://jr-dpg.dpg.army.mil

Homeland Security
Science and Technology

Return on Investment (ROI) Areas

- **Modeling:**
  - Dramatically improved modeling input and validation.
  - Source Terms: model-agnostic, and critical for accurate TIH modeling.
  - Atmospheric Transport and Dispersion (AT&D).
- **Training:**
  - Unique and improved training capabilities – direct impact on emergency responder safety, procedures, and efficiency.
  - Jack Rabbit II products used for guidance and inclusion of TIH scenario in NLE.
- **Emergency Response and Mitigation:**
  - More efficient, focused, and informed emergency response saves money, lives
  - Novel mitigation measures developed, evaluated and validated
  - Improved resource allocation for medical mitigation, response assets
- **Equipment T&E:**
  - Multi-agency co-investment and participation magnifies project value and output
  - Detector and equipment testing at realistic operational conditions
  - Material and electronics exposure testing
- **Evacuation:**
  - Evacuation zone distances and procedures refined through improved modeling
  - Current ERG guidance directs excessive distances (7+ miles) due to modeling uncertainties
  - Realistic distances *dramatically* reduce unnecessary evacuation, impact, costs
  - Results in a significant, quantifiable ROI for evacuation improvement alone

Payoff: DHS

High interest from partners and stakeholders – broad payoff to the Homeland Security Enterprise (HSE)

Capabilities: Field-validation of modeling, and emergency response and urban/environmental impact for chlorine and large-scale TIH releases.

HSE	Payoff
S&T	CSAC: Improved chemical risk assessments (CTRA) and hazard assessments. FRG: Better responder training, guidance, response efficiency, and safety HSARPA: Field-test opportunity for detection systems
TSA	Improved risk assessments (TSRA). Compliance with mandated modeling and security responsibilities *(1519.b of "Implementing Recommendations of the 9/11 Commission Act of 2007").*
FEMA	Inclusion chlorine and/or ***TIH release in 2016 NLE*** with field-validated urban release scenarios. Improved planning and consequence assessment estimation.
OPS	IMAAC: Enhanced hazard predictions and response support *during* large-scale TIH release incidents.
OIP	NPPD-ISCD: Better chemical supply chain hazard and risk assessments, improved implementation of CFATS.
OHA	Improved TIH hazard analyses – more accurate and efficient allocation of medical response resources and planning, worried-well reduction,
USCG	Improved planning and response for barge and port TIH release incidents.

Homeland Security
Science and Technology

Payoff: Interagency

Interagency partners have indicated intent to join effort to advance their organizational missions and mandates

Interagency	Payoff
DOT-PHMSA	Updated ERG modeling will improve accuracy of Protective Action Distances, with ***direct impact on 2016 ERG guidance***.
DOD-DTRA	HPAC/JEM improvement using source term and dispersion data. Enhanced TIH release predictive and support capability for DTRA-Reachback operations
DOD-ECBC	Fulfillment of field-test requirement to validate chlorine and TIH environmental chemical reactions: FY 2014 "Degrade" project
DOD-NGIC	Field validated data and TIH modeling for war-fighter support simulations
DOD-NSWC	Field-validation of RAILCAR source-term engine.
DOD-AFRL	Aircraft material exposure test results with real-time exposure profiles.
NOAA	Improved ALOHA model capability and accuracy for Cl_2 and TIHs
NIST	Capability for outdoor → indoor building contaminant ingestion into CONTAM indoor model, using field-validated infiltration data
"Other"	Unique opportunity for unmanned drone capability testing of chemical cloud identification, mapping, and tracking. Unprecedented real-time aerial footage and shared data.

Homeland Security
Science and Technology

Payoff: Industry/Organizations

Industrial collaboration expanded beyond Jack Rabbit I, seeking to take advantage of this unprecedented testing opportunity

Industry	Payoff
Association of American Railroads	Enhanced railroad security and novel mitigation strategies driven by experimental findings and analyses. Improved guidance and training to member companies.
Chlorine Institute (CI)	Improved industry guidance for chlorine operations and safety for member companies. Updated Chlorine Institute "Pamphlet" series of publications.
American Chemistry Council (ACC)	
International Association of Fire Chiefs (IAFC)	Improved safety and response efficiency of emergency responders. Improved evacuation/shelter-in-place guidance and implementation. Use of release images, footage, and findings for TIH response training programs.
National Fire Prevention Association (NFPA)	
Chemical Detector Developers (RAE, Safer, Smiths, Bruker, etc.)	Unique field-test opportunity for handheld and autonomous chemical detectors – co-located instrumentation and mutual data-sharing greatly expand useful data sets.
Model Developers	Numerous model developers intend to utilize test campaign as definitive source for improvement and validation for TIH capabilities

Homeland Security
Science and Technology

Schedule and Milestones