

# **Research on anhydrous ammonia hazards at HSE and scientific knowledge gaps**

**Simon Gant**

Health and Safety Workshop, First Symposium on Ammonia Energy, Cardiff University, UK, 2 September 2022

**Research** - HSE funded to provide evidence which underpins its policy and regulatory activities

**Guidance** - freely available to help people comply with health and safety law

# Overview

---

- Jack Rabbit III anhydrous ammonia project
  - Review of previous Jack Rabbit I and II projects
  - Outline plans for Jack Rabbit III
  - HSE contribution to JRIII and the Modelers Working Group
- Knowledge gaps
  - Identification of knowledge gaps for future testing in Jack Rabbit III
  - Waterborne transport of ammonia
- Ongoing and future work
- Engagement with stakeholders

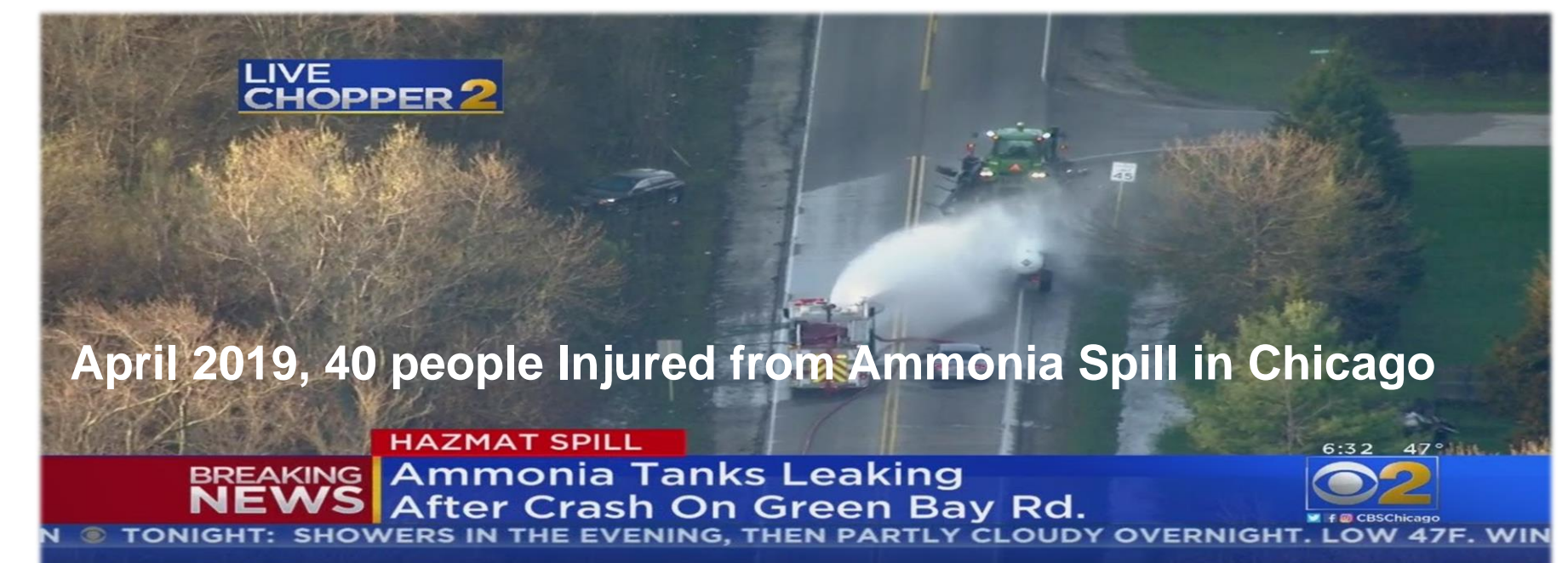


# Jack Rabbit Program

Homeland security enterprise must identify and assess vulnerabilities and consequences of large-scale Toxic Inhalation Hazard (TIH) chemical releases

- Millions of tons of TIH materials are shipped annually throughout the United States
- TIHs such as ammonia are transported in bulk as pressure-liquefied and temperature-liquefied gases via road, water, rail
- An accidental or intentional release can rapidly generate a lethal vapor cloud
- JR I and JR II: 1 to 20-ton  $\text{NH}_3$  and  $\text{Cl}_2$  releases which yielded critical data, findings, and far-reaching impacts (shown below)

Jack Rabbit II Chlorine Testing in 2015 and 2016



<https://www.youtube.com/watch?v=5nmQsY2XkV4>



<https://cen.acs.org/articles/96/i2/Mixed-uncontrolled-chemical-reaction-chlorine.html>

Slide provided by US Department of Homeland Security, Science and Technology, Chemical Security Analysis Center (DHS S&T CSAC)  
Images of Jack Rabbit II trials © DHS S&T CSAC

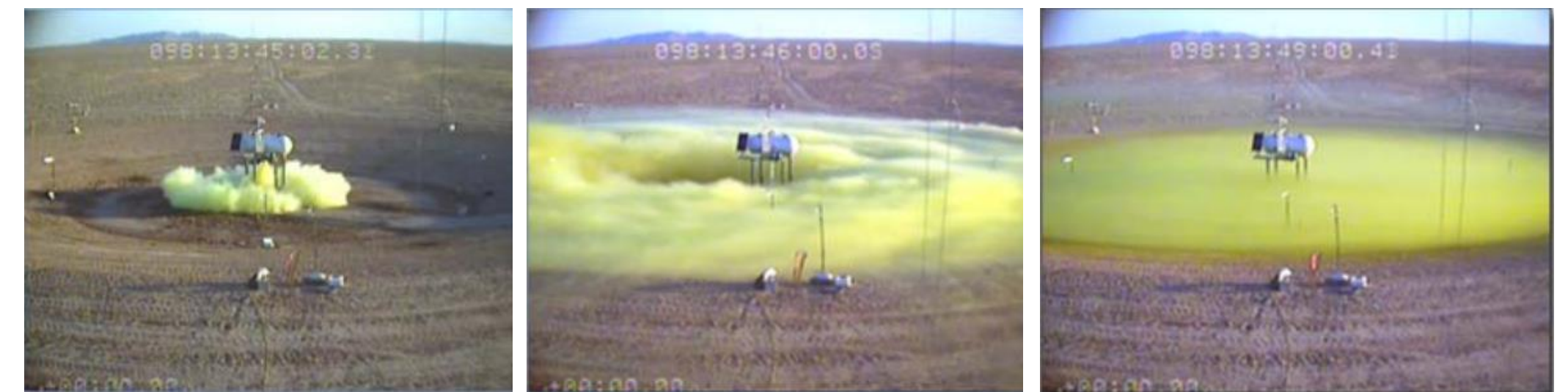


# Jack Rabbit I and II

- **Jack Rabbit program aims:** fill critical hazard prediction data gaps in toxic inhalation hazard chemical release atmospheric dispersion modelling
- **Jack Rabbit I and II impacts:**
  - Improved our understanding of atmospheric dispersion of large-scale, pressure-liquefied chlorine and ammonia releases
  - Informed emergency responders (standoff distances, equipment performance, sheltering)
  - Validated models for sources, dispersion, accumulation in buildings/vehicles through experiments
- **Jack Rabbit I field trials at Dugway Proving Ground, Utah, April/May 2010**
  - 1 and 2 US ton anhydrous ammonia and chlorine release experiments



Ammonia

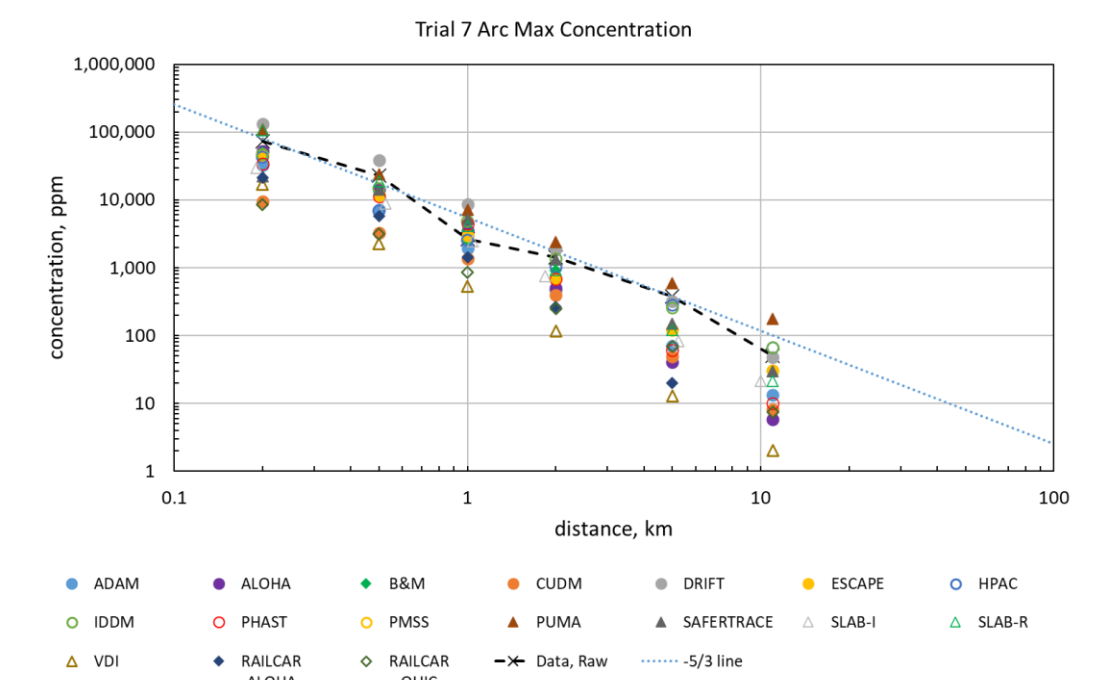
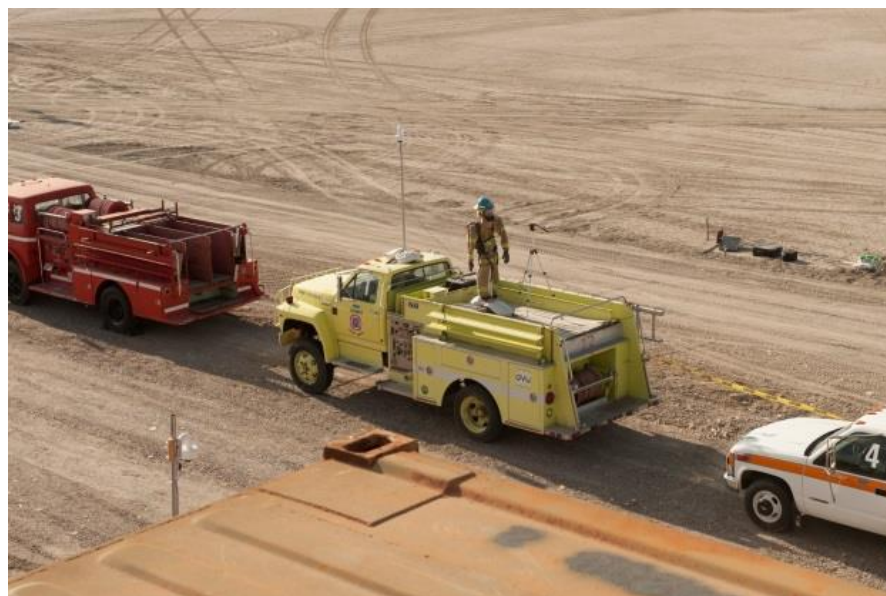
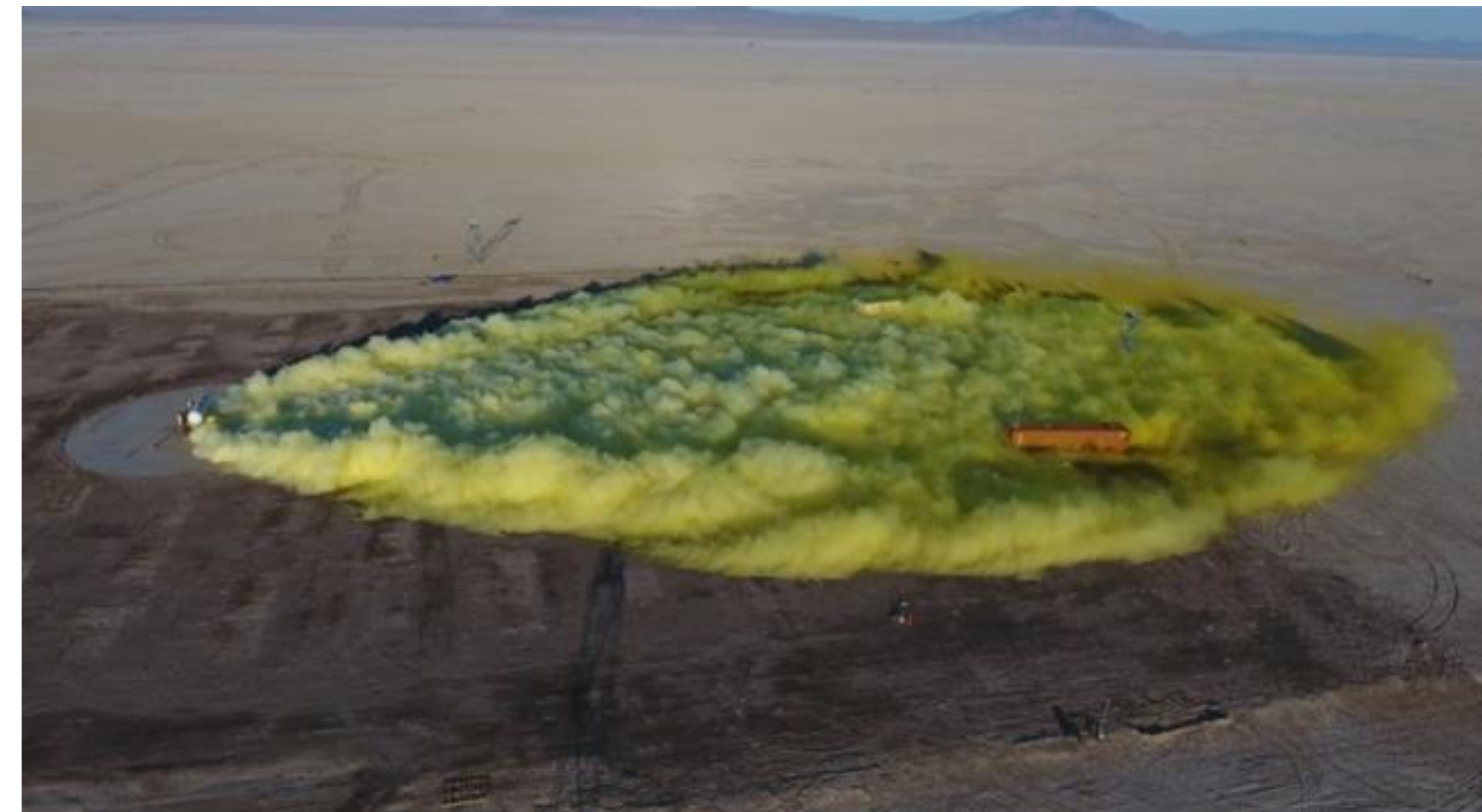


Chlorine



# Jack Rabbit II

- **Jack Rabbit II** field trials at Dugway Proving Ground, Utah, 2015-2016
  - Nine 5 – 20 US ton chlorine release experiments (inc. road tanker release)



For further information, see: <https://www.uvu.edu/es/jack-rabbit/>



# Jack Rabbit II-Strategic Partnerships



## Interagency

DHS – S&T  
DHS – TSA  
DHS – CISA  
DHS – FEMA



## Department of Defense

DTRA  
DARPA  
Defense Threat Reduction  
Agency  
US Army  
CCDC CBC  
Army Test Evaluation  
Command  
DUSA T&E



## U.S. Department of Transportation



Association of American  
Railroads (AAR)

American Chemistry Council  
(ACC)

Multiple Additional Commercial  
Participants and Contributors:

Honeywell Analytics-RAE Systems

Solutions (S<sup>3</sup>) – LIDAR

Signature Science-UV Detector



# Jack Rabbit III

---

- New project focusing on large-scale ammonia releases
- Work activities:
  - Initial hazard characterization exercise
    - Toxic gas hazard mapping
    - Ammonia energy horizon scanning
    - Fertilizer industry and first responder interviews
    - US Nationwide emergency responder survey
  - Surface chemical reactivity laboratory studies with a range of materials
  - Field trials
    - Field study gaps analysis
    - Test site facility surveys and environmental impact assessments
    - Medium and large-scale field trials (perhaps supplemented by wind-tunnel tests)
  - Final reporting: technology and capability transfer
- Tentative timescale: 2021 – 2027



# Jack Rabbit III (2021 – 2027)

---

- Working Groups
  - **Source**, Tom Spicer (University of Arkansas)
  - **Modelling**, Joe Chang (Rand Corporation) and Simon Gant (HSE)
  - **Deposition and surface chemical reactivity**, Steve Hanna (Hanna Consultants)
  - **Human effects**, Sweta Batni and Kierstyn Schwartz-Watjen (DTRA)
  - **Instrumentation**, Bruce Hinds (DTRA)
  - **Data quality**, Tom Mazzola (SPA/DTRA)
  - **Emergency responders**, Andy Byrnes (Utah Valley University)
  - **Waterborne releases**, Matt Ward (Maritime Planning Associates)
- Each group involves a team of experts collaborating with US and international researchers
- Modelers Working Group initial dispersion model inter-comparison exercise, 2021-2022
  - Aim: to understand the accuracy of models that may be used to design the Jack Rabbit III trials, e.g. to design the JRIII sensor array
  - To identify important model input parameters that we may need to carefully assess or measure in the trials



# Jack Rabbit III Modelers Working Group

- Initial dispersion model inter-comparison exercise

## Desert Tortoise



© LLNL

- Nevada Test Site, 1983
- Ammonia discharge rates of 81 kg/s to 133 kg/s
- 81 mm or 95 mm diameter source
- Releases of 10 – 41 tonnes of pressure-liquefied ammonia

## FLADIS



Photo © Kenneth Nyren, FOA  
Source: Hall, Walker & Butler (1999)

- Landskrona test site, Sweden, 1993-1994
- Ammonia discharge rates from 0.25 kg/s to 0.55 kg/s
- 4.0 mm and 6.3 mm diameter orifices

#	Organization	Model
1	Air Products, USA	VentJet
2	BAM, Germany	AUSTAL
3		VDI
4	DGA, France	PHAST v8.6
5		Code-Saturne v6.0
6	DNV, UK	PHAST v8.61
7	DSTL, UK	HPAC v6.5
8	DTRA, ABQ, USA	HPAC v6.7
9	DTRA, Fort Belvoir, USA	HPAC
10	EDF/Ecole des Ponts, France	Code-Saturne v7.0
11		Crunch v3.1
12	Equinor, Norway	PHAST v8.6
13	FFI, Norway	ARGOS v9.10
14	FOI, Sweden	PUMA
15	Gexcon, Netherlands	EFFECTS v11.4
16	Gexcon, Norway	FLACS
17	GT Science & Software	DRIFT v3.7.19
18	Hanna Consultants, USA	Britter & McQuaid WB
19		Gaussian plume model
20	HSE, UK	DRIFT v3.7.12
21		PHAST v8.4
22	INERIS, France	FDS v6.7
23	JRC, Italy	ADAM v3.0
24	NSWC, USA	RAILCAR-ALOHA
25	Shell, UK	FRED 2022
26	Syngenta, UK	PHAST v8.61



# Overview

---

- Jack Rabbit III anhydrous ammonia project
  - Review of previous Jack Rabbit I and II projects
  - Outline plans for Jack Rabbit III
  - HSE contribution and the Modelers Working Group
- Knowledge gaps
  - Identification of knowledge gaps for future testing in Jack Rabbit III
  - Waterborne transport of ammonia
- Ongoing and future work
- Engagement with stakeholders



# Knowledge Gaps

---

- Two collaborative scientific knowledge gaps exercises conducted in 2020 on modelling of toxic industrial chemical releases
- Aim: to take stock of findings from Jack Rabbit I and II and identify remaining knowledge gaps for future testing in Jack Rabbit III
  1. European exercise, coordinated by HSE and DSTL
  2. USA exercise, led by Steve Hanna with support from DHS and DTRA
- The two studies were combined and published jointly:
  - Hanna S., Mazzola T., Chang J., Spicer T., Gant S.E. and Batt R. "Gaps in Toxic Industrial Chemical (TIC) model systems: improvements and changes over past ten years", Process Safety Progress, June 2021. Open Access pdf available from: <http://dx.doi.org/10.1002/prs.12289>
- Topics covered:
  - Definition of scenarios, source models, dispersion (dense gas in low wind speeds, transition to passive dispersion, obstacles and terrain, meteorology, infiltration into buildings, dry deposition and chemical reactivity), health effects



# Knowledge Gaps

## Participants in the European knowledge gaps exercise:

1. Maxime Nibart and Jacques Moussafir, **ARIA Technologies**, France
2. Karim Habib, **BAM**, Germany
3. Kieran Glynn and Felicia Tan, **BP**, UK
4. Patrick Armand, **CEA**, France
5. Catheryn Price and David Carruthers, **CERC**, UK
6. Silvia Trini Castelli, National Research Council (**CNR**), Italy
7. Alexandros Venetsanos, National Centre for Scientific Research “**Demokritos**”, Greece
8. Mike Harper, **DNVGL** Software, UK
9. Bertrand Carissimo, Électricité de France (**EDF**), France
10. Thomas Vik and Anders Helgeland, Forsvarets Forskningsinstitut (**FFI**), Norway
11. Ari Karppinen, Finnish Meteorological Institute (**FMI**), Finland
12. Oscar Björnham, Totalförsvarets Forskningsinstitut (**FOI**), Sweden
13. Kees van Wingerden and Lorenzo Mauri, **Gexcon** AS, Norway
14. Graham Tickle, **GT Science and Software** Ltd, UK
15. Jean-Marc Lacome and Benjamin Truchot, **INERIS**, France
16. Colin Brunold, **INOVYN** ChlorVinyls Limited, UK
17. Luciano Fabbri, European Commission Joint Research Centre (**JRC**), Italy
18. Andreas Mack and Mark Spruijt, the Netherlands
19. Claire Witham and Susan Leadbetter, **Met Office**, UK
20. James Stewart-Evans, Public Health England (**PHE**), UK
21. Eelke Kooi and Bert Wolting, **RIVM**, the Netherlands
22. Chris Dixon, **Shell**, UK
23. Stephen Puttick, **Syngenta**, UK
24. John Zevenbergen, **TNO**, the Netherlands
25. Delphine Laboureur and Sophia Buckingham, von Karman Institute for Fluid Dynamics (**VKI**), Belgium



# Knowledge Gaps: Ammonia Spills on Water

- Only one experimental waterborne ammonia spill dataset, by Raj *et al.* (1974)

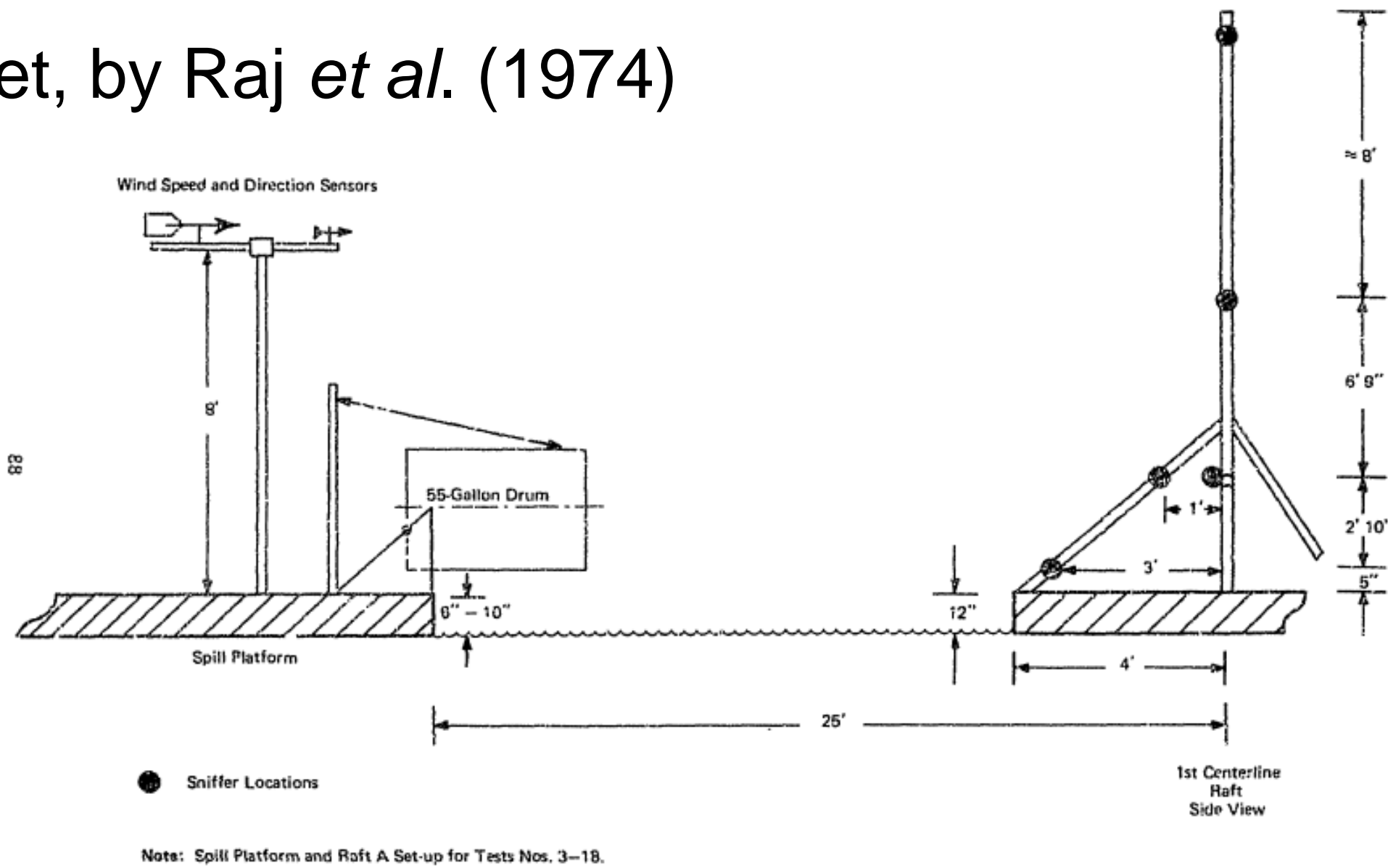
PREDICTION OF HAZARDS OF SPILLS OF ANHYDROUS  
AMMONIA ON WATER

PREPARED FOR      ARTHUR D. LITTLE, INCORPORATED  
COAST GUARD        MARCH 1974

Raj, P.K., Hagopian, J., and Kalelkar, A.S.

The vapor puff formed is very buoyant and rises into the air as it travels downwind. The rate of rise depends on the wind velocity. Under low wind conditions the cloud forms a characteristic mushroom cloud before dispersing. The path of the cloud can be estimated with reasonable accuracy by existing plume theories. Because of the rapid rise in low wind, the toxic hazard at ground level is smaller for low wind than for high wind.

<https://apps.dtic.mil/sti/pdfs/AD0779400.pdf>



1.3.1	Laboratory Experiments	
1.3.1.1	Surface Spills	½ US gallon (2 litre)
1.3.1.2	Underwater Release	
1.3.2	Intermediate-Scale Experiments	
1.3.2.1	Surface Spills	
1.3.2.2	Underwater Release	5 US gallon (20 litre) in swimming pool
1.3.3	Large-Scale Experiments	
1.3.3.1	Surface Spills	
1.3.3.2	Underwater Release	50 US gallon (0.2 m³) in lake

# Knowledge Gaps: Ammonia Spills on Water

- HSE Report by Griffiths (1977) critical of conclusions drawn from Raj *et al.* (1974) tests
  - “... does not provide the information needed to perform hazard assessments of LNH<sub>3</sub> releases on water”
- Concluded that further experiments are needed



## CRITICAL REVIEW OF THE USCG REPORT BY RAJ ET AL (1974) ON SPILLS OF LIQUID ANHYDROUS AMMONIA ON TO WATER, WITH AN ALTERNATIVE ASSESSMENT OF THE EXPERIMENTAL RESULTS

R. F. Griffiths

January 1977

### SUMMARY

This report is principally devoted to a criticism of experiments performed by Raj et al (Reference 10) in which it was demonstrated that spills of LNH<sub>3</sub> (liquid anhydrous ammonia) on to water from refrigerated storage tanks result in releases of ammonia to the atmosphere. Raj et al concluded that such releases are adequately described in terms of a buoyant plume rise model, in which it is assumed that the ammonia is released as a pure undiluted vapour.

This conclusion is challenged on the grounds that it is incompatible with the experimental measurements. An alternative interpretation of the data is proposed which is shown to be consistent with the observed behaviour. In this scheme the ammonia is considered to be released as a plume containing both vapour and liquid droplet aerosol, by virtue of which it is rendered non-buoyant.

The difficulties inherent in providing a rigorous description of such a release are circumvented by use of a simplified model of the dispersion behaviour, which is used to calculate downwind ground level concentrations (GLC) of ammonia vapour. Comparison calculations are performed to demonstrate that the hazard ranges for a given consequence are significantly greater if the release is non-buoyant.

It is concluded that the study performed by Raj et al does not provide the information needed to perform hazard assessments for LNH<sub>3</sub> releases on to water, and that further experimental studies are required.



# Overview

---

- Jack Rabbit III anhydrous ammonia project
  - Review of previous Jack Rabbit I and II projects
  - Outline plans for Jack Rabbit III
  - HSE contribution and the Modelers Working Group
- Knowledge gaps
  - Identification of knowledge gaps for future testing in Jack Rabbit III
  - Waterborne transport of ammonia
- Ongoing and future work
- Engagement with stakeholders

# Ongoing and Future Work

- Jack Rabbit III
  - Publishing results from Desert Tortoise and FLADIS exercise at 21<sup>st</sup> International Conference on Harmonisation within Atmospheric Dispersion for Regulatory Purposes, 27-30 Sept 2022
  - Preparing follow-on modelling exercise on previous large-scale ammonia incident
  - Initial simulations to support design of future JR III trials (pipeline release configuration)
  - Discussions ongoing with stakeholders, potential sponsors and test sites
  
- HSE review of ongoing risk studies on green ammonia infrastructure
  - Lloyds Register study of hydrogen and ammonia infrastructure, 2020<sup>1</sup>
  - DNV Port of Amsterdam study on bunkering of alternative marine fuels<sup>2</sup>
  - ITOCHU Joint Study Framework on Ammonia as an Alternative Marine Fuel
  - Ongoing DNV-led study for Global Centre for Maritime Decarbonisation (Singapore)

1) <https://static1.squarespace.com/static/5d1c6c223c9d400001e2f407/t/5eb553d755f94d75be877403/1588941832379/Report+D.3+Safety+and+regulations+Lloyds+Register.pdf>

2) [https://sustainableworldports.org/wp-content/uploads/DNV-POA-Final-Report\\_External-safety-study-bunkering-of-alternative-marine-fuels-for-seagoing-vessels\\_Rev0\\_2021-04-19.pdf](https://sustainableworldports.org/wp-content/uploads/DNV-POA-Final-Report_External-safety-study-bunkering-of-alternative-marine-fuels-for-seagoing-vessels_Rev0_2021-04-19.pdf)



# Engagement with Stakeholders

---

- Aim of this HSE Science Division engagement at the First Symposium on Ammonia Energy is to learn about:
  - Organisations pursuing green ammonia projects (UK projects mainly, but also internationally)
  - Project timescales, scope and budgets
  - Identification of scientific knowledge gaps related to ammonia hazard and risk studies
  - Any ongoing scientific studies to address knowledge gaps
- Questions related to HSE policy and regulation will need to be followed-up later by other HSE colleagues
- Jack Rabbit III
  - If organisations would like further information on Jack Rabbit III, or would like to get involved, HSE can help to put them in touch with the US project coordinators
  - Particular interest in establishing contact with potential partners for conducting new waterborne ammonia spill experiments

# Acknowledgements

---

- Many thanks to US Department of Homeland Security, Science and Technology, Chemical Security Analysis Center for use of copyright Jack Rabbit I, II and III material and for contributions to these slides
- Contact email: [simon.gant@hse.gov.uk](mailto:simon.gant@hse.gov.uk)

## Thank you

- The contents of this presentation, including any opinions and/or conclusions expressed, are those of the author's alone and do not necessarily reflect HSE policy



---

# Extra Material

# **Identification of knowledge gaps for future testing in Jack Rabbit III: a European perspective**

**Simon Gant<sup>1</sup>, Rachel Batt<sup>1</sup>, Steven Herring<sup>2</sup> and Harvey Tucker<sup>1</sup>**

<sup>1</sup> Health and Safety Executive (HSE), Buxton, UK

<sup>2</sup> Defence Science and Technology Laboratory (DSTL), Porton Down, UK

**24<sup>th</sup> Annual George Mason University Conference on Atmospheric Transport and Dispersion Modeling  
December 8-10, 2020**

**Research** - HSE funded to provide evidence which underpins its policy and regulatory activities

**Guidance** - freely available to help people comply with health and safety law



# 1. Two-phase jets

---

- Critical issue studied in several previous projects (see later review)
- Lack of data for partitioning between airborne aerosol and liquid pool (i.e. rainout fraction)
- Validity of rainout approaches in operational models is uncertain
- Rainout fraction can have significant influence on dispersion, particularly in the near field
- Rainout is scale-specific: depends on geometry and release size
- Useful to consider range of conditions: hole sizes, release orientations, impinging, short releases (e.g. catastrophic vessel failure), long duration releases (e.g. pipeline)
- Uncertainty in post-expansion source conditions: jet velocity and liquid fraction (metastable or homogeneous equilibrium) – could be studied in laboratory-scale tests?
- Uncertainty in behaviour inside vessel (champagne effect)

## 2. Obstacles

---

- Limited field-scale data available for dense-gas dispersion with realistic obstacles
- At what size do obstacles become important such that they need to be taken account of in modelling?
- Are dense gas dispersion models for flat and rough terrain still applicable to built-up environments?
- Which is better: a building-resolved passive model or a dense gas model with surface roughness?
- How much do isolated or small obstacles affect dispersion?
- What is the impact of obstacles on persistence of the cloud?
- How effective are vapour barriers for mitigation?
- Do wakes from isolated tall buildings in city environments have a significant affect? Is it important to model them?



## 3. Transition from dense-gas to passive dispersion

---

- When is it necessary to use a dense-gas model instead of a passive model?
  - Is the current rule of thumb that says a dense-gas model should be used for releases of 1 ton or more accurate?
- Can testing determine if there is a threshold release size when a passive model is adequate?
- How rapid is the mixing between the dense cloud and the atmosphere that produces a passive cloud?
- Does near-field dense gas behaviour matter far downwind?
- How does the transition from dense to passive affect turbulence levels and toxic dose (non-linear toxic response to concentration)?
- What are the implications for infiltration into buildings, e.g. draining of dense clouds into basements?

## 4. Dispersion in low/zero wind speeds

---

- Lack of experimental data for large dense-gas releases in low/zero wind speeds
  - But there are examples of several severe incidents involving flammable dense-gas releases in low/zero wind, e.g. Buncefield and San Juan fuel storage depots
- How do obstacles and terrain influence the dispersion behaviour when the wind speed approaches zero?
- What are the implications of low/zero wind speeds for emergency response?
  - ERG provides protective action distance in downwind direction
  - ERG for ammonia has three wind speeds (low, moderate, high) for (<10 km/h, 10-20 km/h, >20 km/h)
  - What is the advice for very low or zero wind? Which direction is downwind? Are the ERG distances still valid?



## 5. Terrain effects

---

- Lack of experimental data for large dense-gas releases with terrain
  - Indications from incidents that even moderate slopes could have significant effect in low/zero wind
- At what scale does terrain become important for dispersion?
- What is the combined effect of the wind, the release direction and terrain on dense-gas releases?
  - Useful to have range of tests: e.g. releases upslope, downslope and cross-winds for a range of release sizes and slopes
  - Also elevated releases, e.g. for rooftop-mounted ammonia refrigeration tanks

# Jack Rabbit

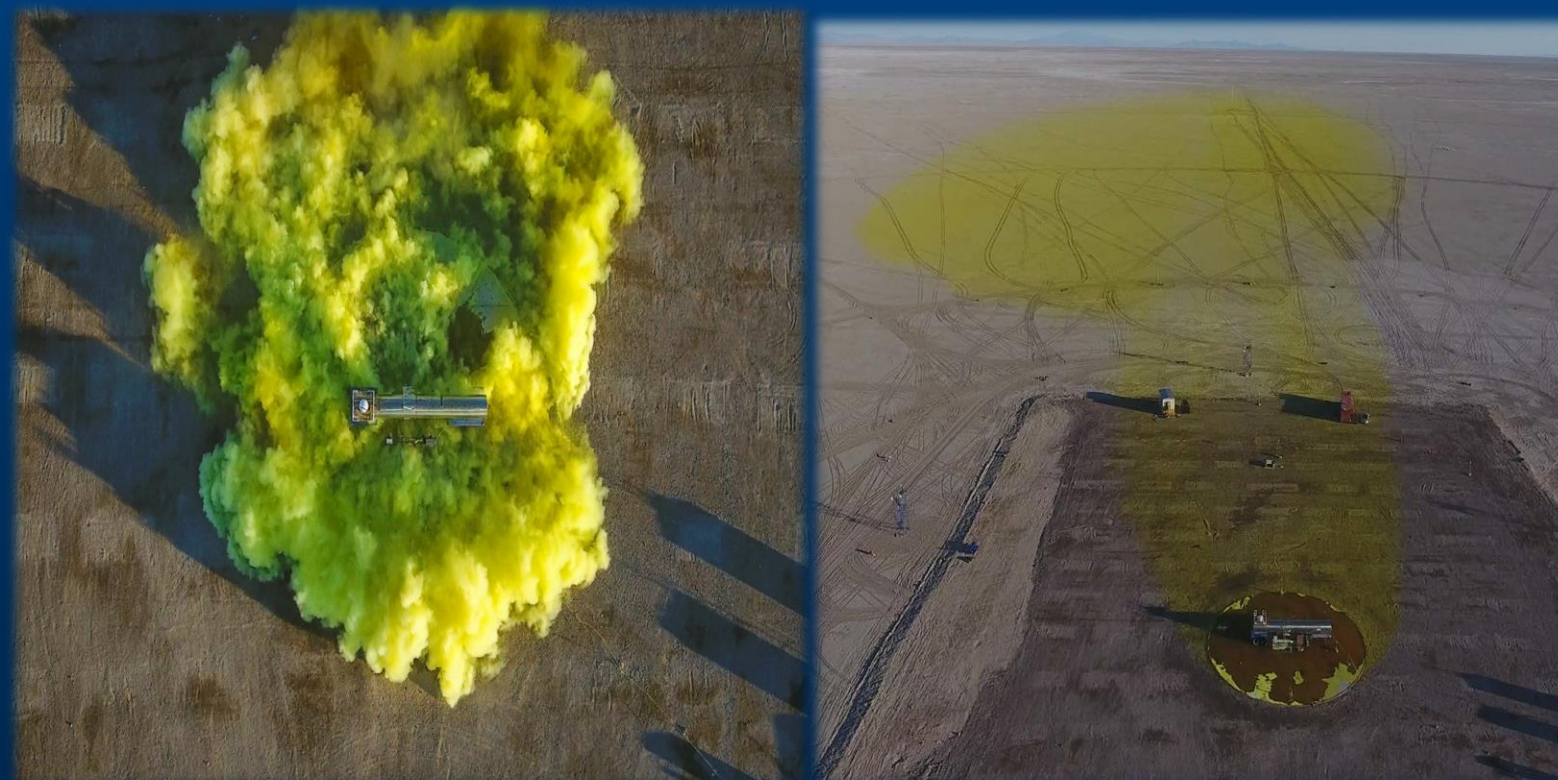
## JR I

Chlorine & ammonia  
basin releases of  
1-2 tons (2010)



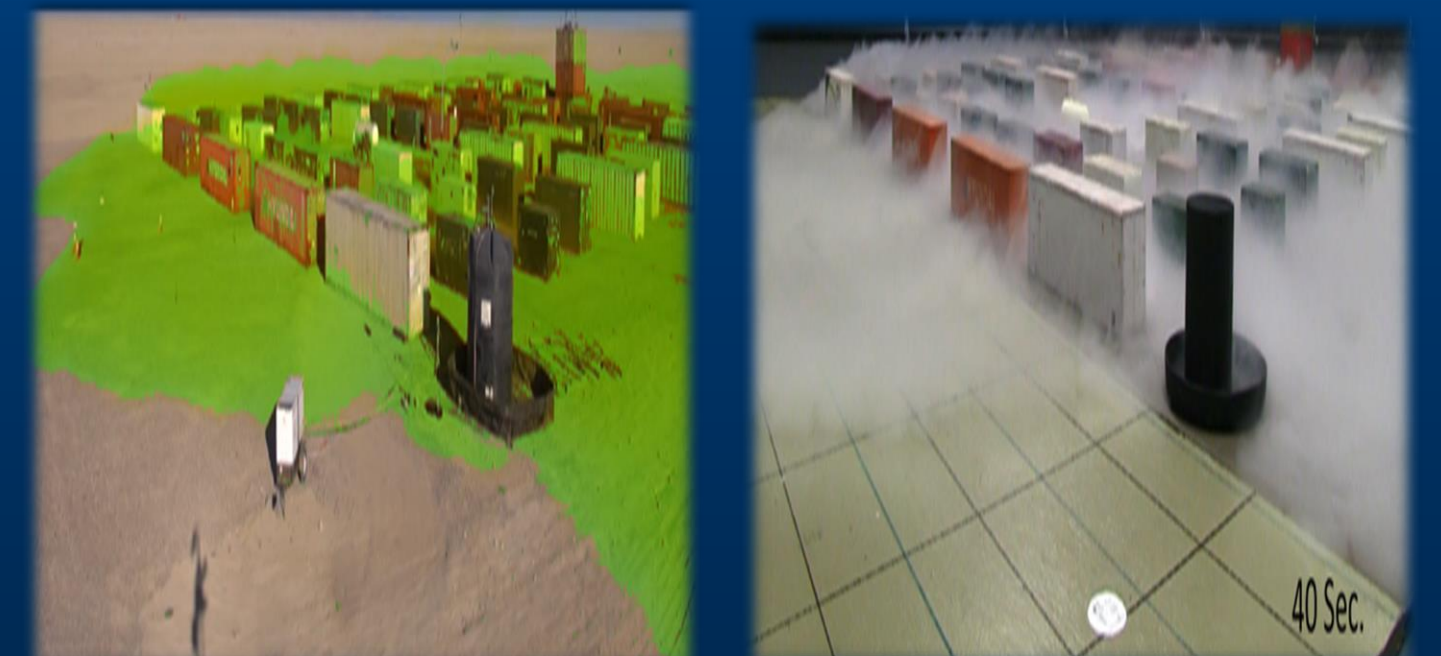
## JR II

Large-scale outdoor  
chlorine releases of  
5-10 tons (2015)  
&  
10-20 tons (2016)



## JR III

Research, analysis,  
laboratory experiments,  
modeling, and field trials





# Jack Rabbit I

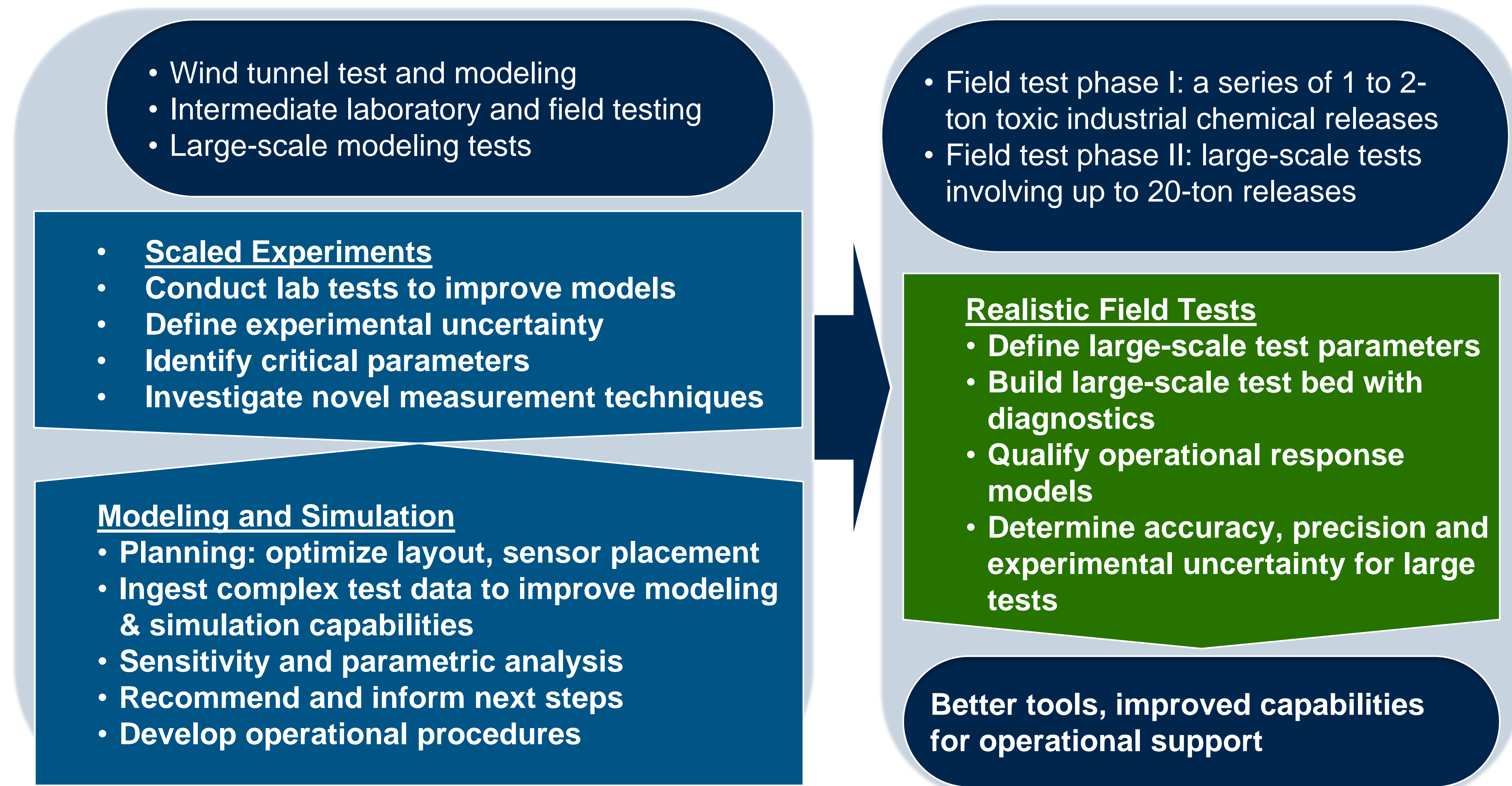
Ammonia Basin Release

Chlorine Basin Release

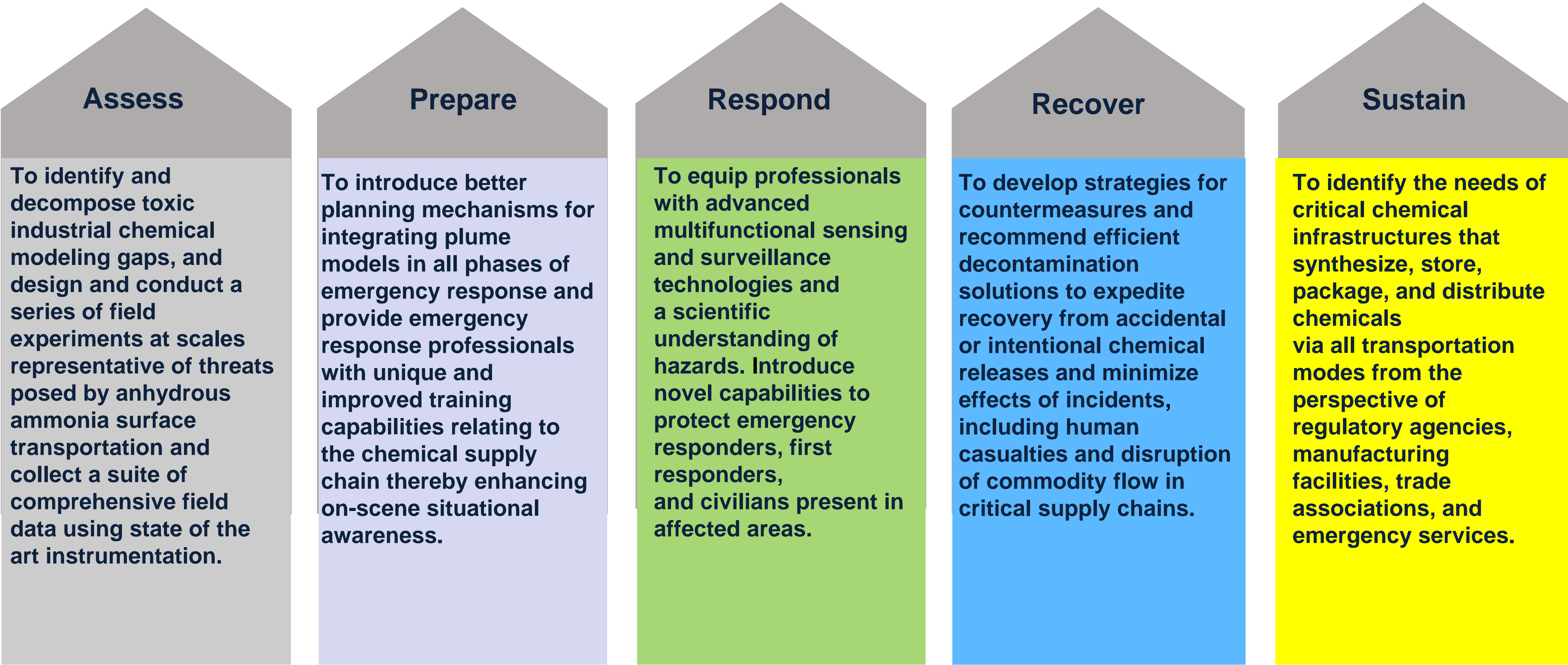




# Jack Rabbit III Strategic Research Approaches



# Jack Rabbit III Objectives



# **Jack Rabbit III Collaborative Research and Development**

**DHS CWMD, CISA, FEMA, TSA, and USCG**

**U.S. DoD DTRA, Army, NSWC & U.S. EPA**

**First Responders**

**Department of Energy Laboratories**

**Fertilizer Industries and Trade Associations**

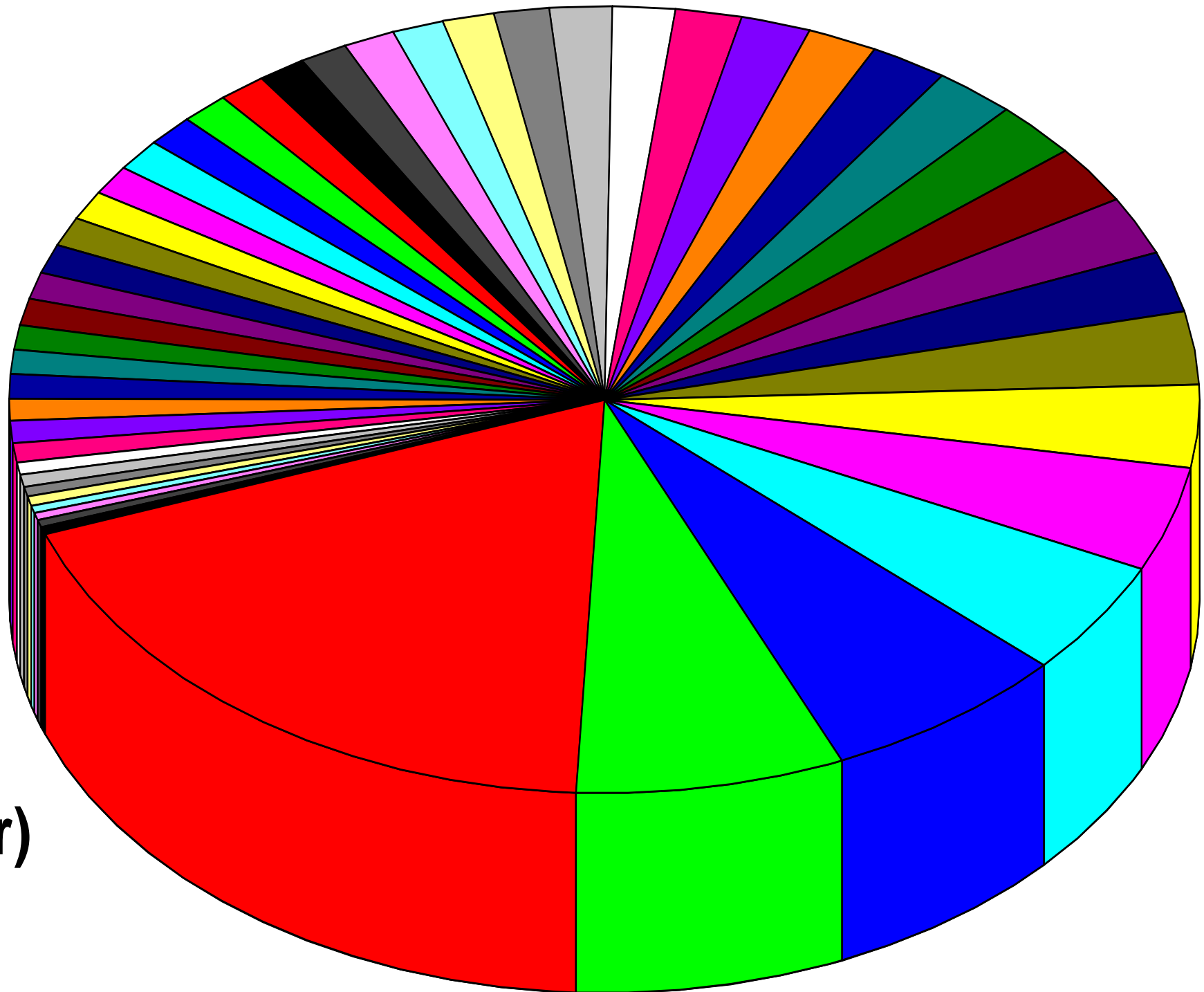
**Academia**

**International Agencies (UK lead by HSE, ROK, Canada, Sweden)**



# Jack Rabbit III Compound of Interest: US Chemical Hazard Characterization

- 19% Ammonia (Anhydrous)
- 7% Hydrogen Sulfide
- 7% Chlorine (Anhydrous)
- 5% Hydrogen Cyanide
- 4% Hydrogen Selenide
- 3% Ammonia (conc. 20% or greater)



### Consequences

Injuries , Accidents, and Property Damage Costs  
Data Source: Risk Management Plan Database from the Right-to-Know Network

### Likelihood

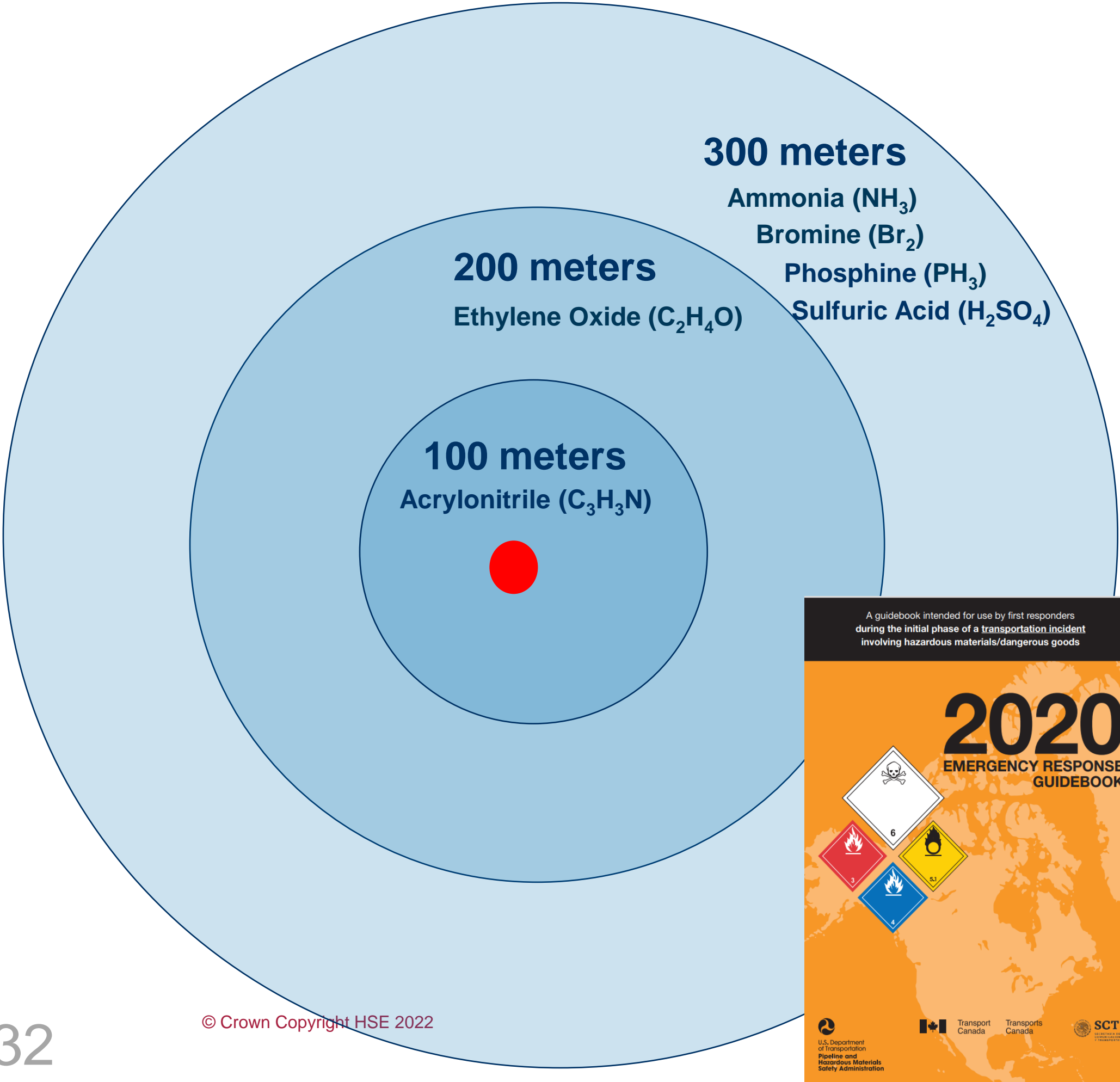
Supply Chain Transportation Volume  
Data Source: CSAC Chemical Risk Assessment - Chemical Transportation Amounts

### Hazards

Toxicity (AEGL), Vapor Pressure, ERG Isolation Distance, and Flammability

# Jack Rabbit III: science driven emergency planning, preparedness, and public awareness

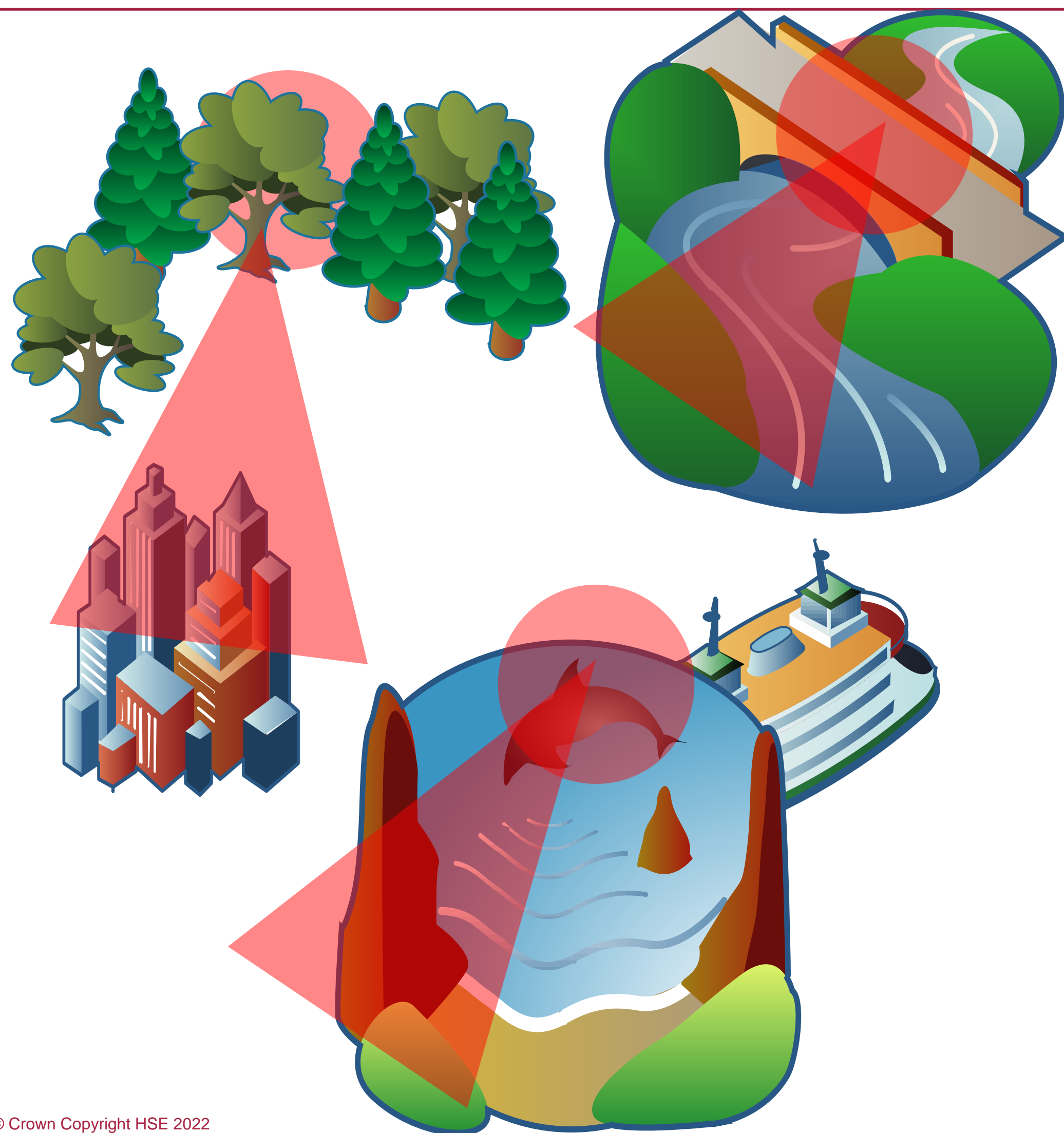
## Initial Isolation Distance for Large Spills



Health effect	Anhydrous Ammonia Concentration (ppm)						
	1	10	100	1,000	10,000	100,000	1,000,000
Mild irritation to upper respiratory track: pungent odor threshold (> 5 ppm)		Odor					
Moderate irritation to eyes, nose, throat, and chest: OSHA PEL: 8-hr TWA		50 ppm					
Serious, irreversible effects: ERPG-2 (1 hour)			150 ppm				
Life-threatening effects, intense irritation, excessive lacrimation: NIOSH IDLH				300 ppm			
Serious lung damage, death if not treated: emergency entry with level A & B PPE level					1,000 ppm < Level A or B PPE		
Burning, blistering of skin: emergency entry with level C PPE					300 ppm < Level C		
Flammability threat: fire and explosion hazard (NOTE: threshold will be lower if mixed with oil)						15-28%	
Immediately fatal to humans: pure anhydrous ammonia gas							<100%

# Jack Rabbit III Scenarios and Approaches Addressing Gaps in Ammonia Release Emergency Response

RESEARCH AND  
GUIDANCE FROM



- Release from a pressurized tank
  - Source term emission models
  - Health risk models
  - Effects from obstacles, terrain, meteorological conditions
  - Ground types: organic or inorganic soils, asphalt, concrete
- Release from a pressurized pipeline
  - Leak at a valve or above ground, small and large amounts
  - Source term emission models
- Release from a refrigerated barge
  - Source term of non-pressurized, cold ammonia release
  - Proportion of downwind over-the-water dispersion versus underwater release
  - Waterborne transport hazards



# Wind Tunnel Model

Jack Rabbit II field trial 1



Flow visualization of the physical scaled model





# Ammonia Supply Chain Infrastructure

## Synthesis

Traditional ammonia uses natural gas/coal and contributes to carbon emissions

CO<sub>2</sub>-free ammonia value chain:

- Green ammonia production using renewable energy: net zero carbon
- Blue ammonia using methane - sequester carbon byproduct

## Storage & Transportation

Land:  
Pipeline, rail, and trucking

Marine shipping: fuel cells, bunkering hubs, and ship-to-ship bunkering

Refrigerated (ocean) vs. pressurized (land)

## Selected Market Applications

Land:

- Agriculture
- Refrigerants
- Water treatment

Ocean:

- Maritime
- Potential CO<sub>2</sub>-free energy carrier