Major Science Issues in Atmospheric Transport and Dispersion Modeling of Accidental Releases of Ammonia to the Atmosphere

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New and Old in the Ammonia World 2017

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My Narrow Area of Expertise

- The assessment of the effects of an ammonia release requires experts in a broad range of topics and a comprehensive modeling system, including scenario description, emissions estimation, atmospheric **transport and dispersion (ATD) simulation**, exposure assessment, and health risk assessment
- My expertise resides in the **bolded** area
- I assume that “somebody” provides me with the characteristics of the emissions as they enter the ambient atmosphere, and that “somebody” will take my outputs of concentration distributions to assess exposure and risk

Topics to be Covered (1)

- Initial ammonia plume behavior for a refrigerated release (buoyant gas) versus a pressurized liquefied gas release (dense two-phase mixture)
- Effects of ambient stability and inversions
- Interactions of cloud with ambient water vapor and/or fog drops
- Removal by chemical reactions and deposition
- Cloud behavior after buoyancy effects become insignificant

Topics to be Covered (2)

- Influence of variations in underlying surface and topography
- Differences between operational (emergency response) and research applications of ATD models (input data!)
- Pros and cons of widely used ATD models
- Evaluations of ATD models with ammonia field data

Buoyant vs dense plume

- The important factor is the difference between the plume and the ambient air density
- Density is influenced by temperature, Molecular Weight MW, fractions of pollutant gas and liquid (embedded small drops)

Initial ammonia plume behavior

- If stored as <u>refrigerated liquid</u> (at -34C)
  - Liquid spill, followed by evaporation
  - Initial plume is buoyant ammonia gas
  - Plume rise formulas are well known
- If stored as <u>pressurized liquefied gas</u>
  - Two-phase (gas-liquid) jet with tiny aerosols
  - Initial plume is dense because of aerosols
  - Could be dense gas slumping (depends on mass release rate, wind speed, and cloud size)
  - If pointed up, jet could rise and then slump to ground. If pointed down, dense wall jet

Buoyant plume rise from a typical oil-fired power plant. The plume is warmer than air

Visible white cloud is fog water, whose density is very small and not enough to decrease the plume rise

JR II Trial 8 dense Cl_2 plume about 30 s after release. Maximum plume rise is about 40 m

Is the ammonia plume from a refrigerated liquid spill buoyant or dense?

- For ammonia, with a molecular weight much less than that of air, an initial gas plume will always be buoyant, no matter what the ambient temperature and water content.
  - For example, evaporation of ammonia gas from a refrigerated liquid spill
  - Plume rise depends on mass evaporation rate. For large spills, the plume rise can be large (>100 m). The bottom of the plume does not diffuse to the ground until distances > about 1 km.

Effects of ambient stability and inversions

- The atmosphere is usually unstable on sunny days and stable on clear nights. It is neutral during cloudy or windy hours
- Turbulence and dispersion are greater during unstable than stable conditions
- An inversion is when T increases with height. Strong inversions (i.e., increased stability) can decrease plume rise and dispersion

Interactions with ambient water vapor and/or fog drops

- Atmospheric chemists say that there is little or no reaction of water vapor (gas phase) with ammonia gas.
- Despite how thick the fog looks, the mass of water in a typical fog is only about 0.1 % of the mass of the ambient air in which the fog is located. Atmospheric chemists say that these drops can absorb some ammonia gas.

Removal by chemical reactions and deposition

- As a result of chemical reactions, some ammonia gas would be removed from the plume, but the ammonia ion would still be present
- Reaction rates (most half lives are more than a few hours) are used in regional air pollution models. The primary long term ammonia source is barnyards and fertilized fields
- Deposition (to the surface) will remove some of the ammonia from the plume. Deposition can be relatively large for vegetated surfaces.

Cloud behavior after buoyancy effects become insignificant

- As the ammonia cloud is dispersed by ambient air, its concentration becomes so low that the total cloud buoyancy (positive or negative) is very small
- Dispersion then proceeds as if the cloud has neutral buoyancy. All ATD models account for this behavior.

Influence of variations in underlying surface and topography

- There is more mixing (and reduced concentrations) over rougher surfaces
- Topography can influence ATD, with effects varying with stability. The hills can channel the air flow. Dense gases released at ground level can initially “flow downhill”.

Main difference between operational and research ATD model applications

- Operational – requires quick response with minimal input data
- Research, Planning, or Historical Analysis – can be done at a leisurely pace

Pros and Cons of widely used ATD hazardous gas models (from 2008 JHM paper on six ATD models compared for three real chlorine railcar accidents: Graniteville, Macdona, and Festus)

All involved pressurized liquefied gas

Festus, Mo

Note shallow yellow chlorine cloud

Source: US Chemical Safety and Hazard Investigation Board

- **Proprietary models** - TRACE and PHAST. Both models calculate source emission rates and downwind dispersion
- **Publicly-available models** – SLAB, HGSYSTEM, ALOHA, and SCIPUFF – generally focus on transport and dispersion, although ALOHA has source emissions capabilities and HGSYSTEM can calculate a release from a hole in a pressurized vessel.

ALOHA

- Part of CAMEO. Its dense gas model is a simplified version of DEGADIS. Distributed by the EPA and NOAA. In use by most fire departments in the U.S.
- Has simplified source emissions algorithms for most types of sources. Makes decisions internally about rainout etc. that are not necessarily consistent with current knowledge
- Decides internally about which algorithm to use (hard-wired) and the user has little control.
- ***To be conservative, does not allow plume rise***.
- Has been evaluated with field data from ground level dense gas sources

Major point - ALOHA is the only model in the group of six models that does not allow plume rise and assumes the plume centerline remains at ground level

- It is well-recognized that buoyant plumes will rise, as shown in my earlier section on plume rise.
- As a result of plume rise, the center of the plume can be 100 m or more above ground, thus greatly reducing ground concentrations

HGSYSTEM

- Developed by Shell
- Distributed by EPA, API, and Shell. The science is excellent. It has a jet module and an evaporating pool module, as well as an instantaneous box model
- Has been extensively evaluated with field data and demonstrated to provide good performance
- Similar to DEGADIS in many ways

PHAST

- Proprietary model from DNV in wide use
- Handles releases from jets or area sources, as well as instantaneous releases
- Has source emissions algorithms – updated recently for jets from pressurized liquefied gases, as result of studies sponsored by European industry-agency consortiums.
- Has been extensively evaluated with field data and demonstrated to provide good performance

SCIPUFF

- Lagrangian puff model developed in the 1980’s
- Greatly enhanced in the 1990’s and 2000’s under DOD and DHS support, and is the ATD module in the HPAC system
- Has dense gas, aerosol and simple chemistry algorithms. Extensively evaluated with field data and has good performance
- Can treat continuous, instantaneous and finite duration releases.
- Has excellent liquid pool evaporation algorithms. Research versions use advanced drop size equations for two-phase jets.

SLAB

- Developed by DOE/LLNL to address effects of dense clouds from evaporating pools resulting from LNG releases. Can handle horizontal jets
- Is a basis for the EPA RMP rules
- The science is excellent. Its equations for handling finite duration releases are used by many other models
- Source emissions inputs must be provided by user
- Extensively evaluated with field data and demonstrated to provide good performance

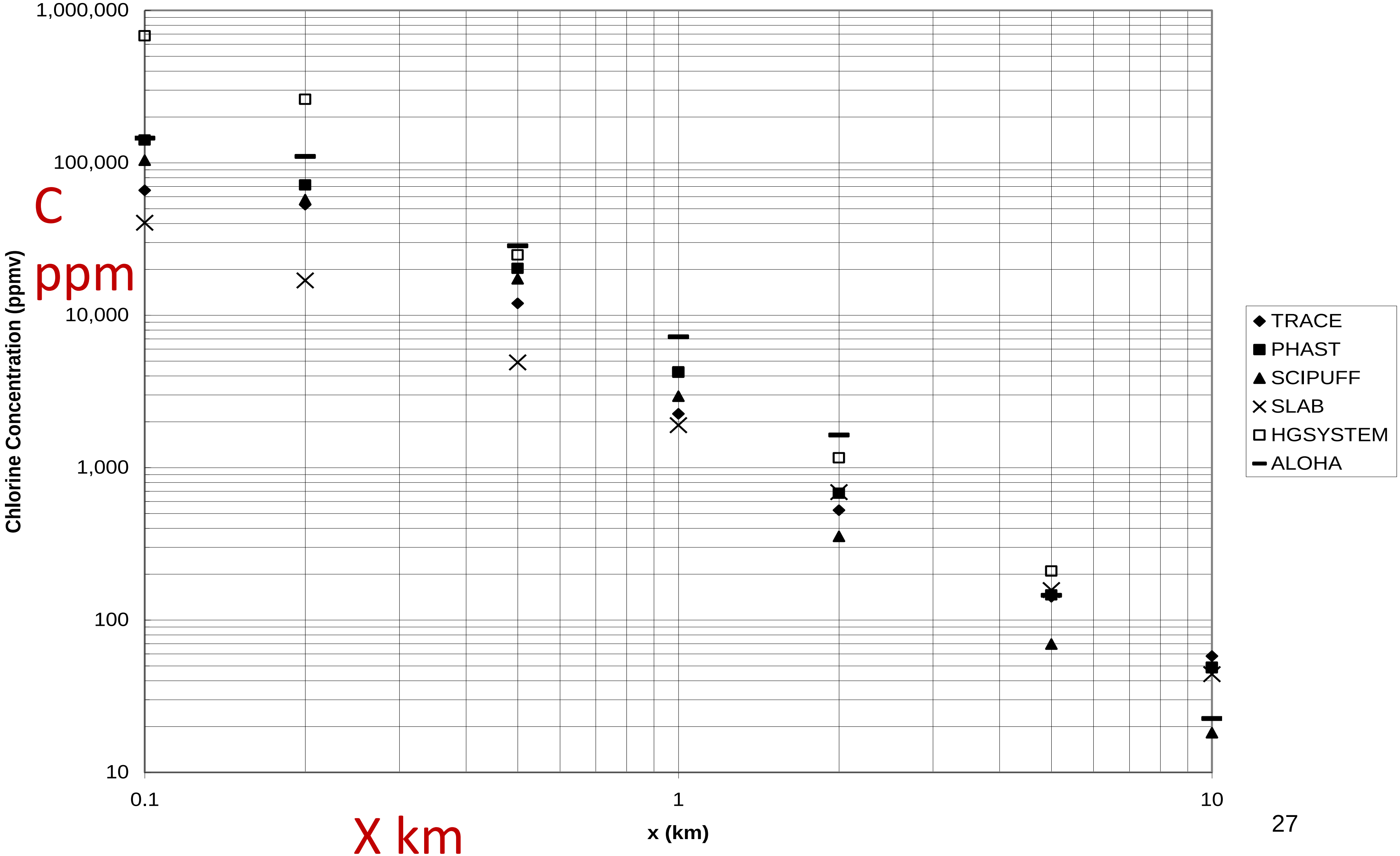
TRACE

- Proprietary model from SAFER in wide use
- Handles releases from jets or area sources, as well as instantaneous releases
- Has state-of-art source emissions algorithms.
- Has been extensively evaluated with field data and demonstrated to provide good performance

Performance Measures Shown here

- Predictions of C vs x for each model on the same figure
- It is stressed that it is not known which model is “best” when compared with observations. There are no C observations at the three sites. It is possible that the outlier model is “best”.

Six model comparisons of predictions for Graniteville chlorine release



C ppm

X km

Conclusions

- Most of the time, the six models’ simulations of cloud centerline concentration agree with each other within plus and minus a factor of two
- There are no observed concentrations to use to check the models

Evaluations of ATD Models with Ammonia Field Data

- Overview of field experiments (Desert Tortoise and Jack Rabbit I) involving pressurized liquefied gases
- Some results of DT model evaluations (Hanna et al. 1991 JHM 26, 127-158
- Overview of ammonia field experiments involving liquid spills (a few old data sets, such as Frie et al 1992)

Setup for 1983 Desert Tortoise Anhydrous Ammonia Field Experiment (Pressurized Liquefied Gas with Nitrogen Pad to maintain pressure)

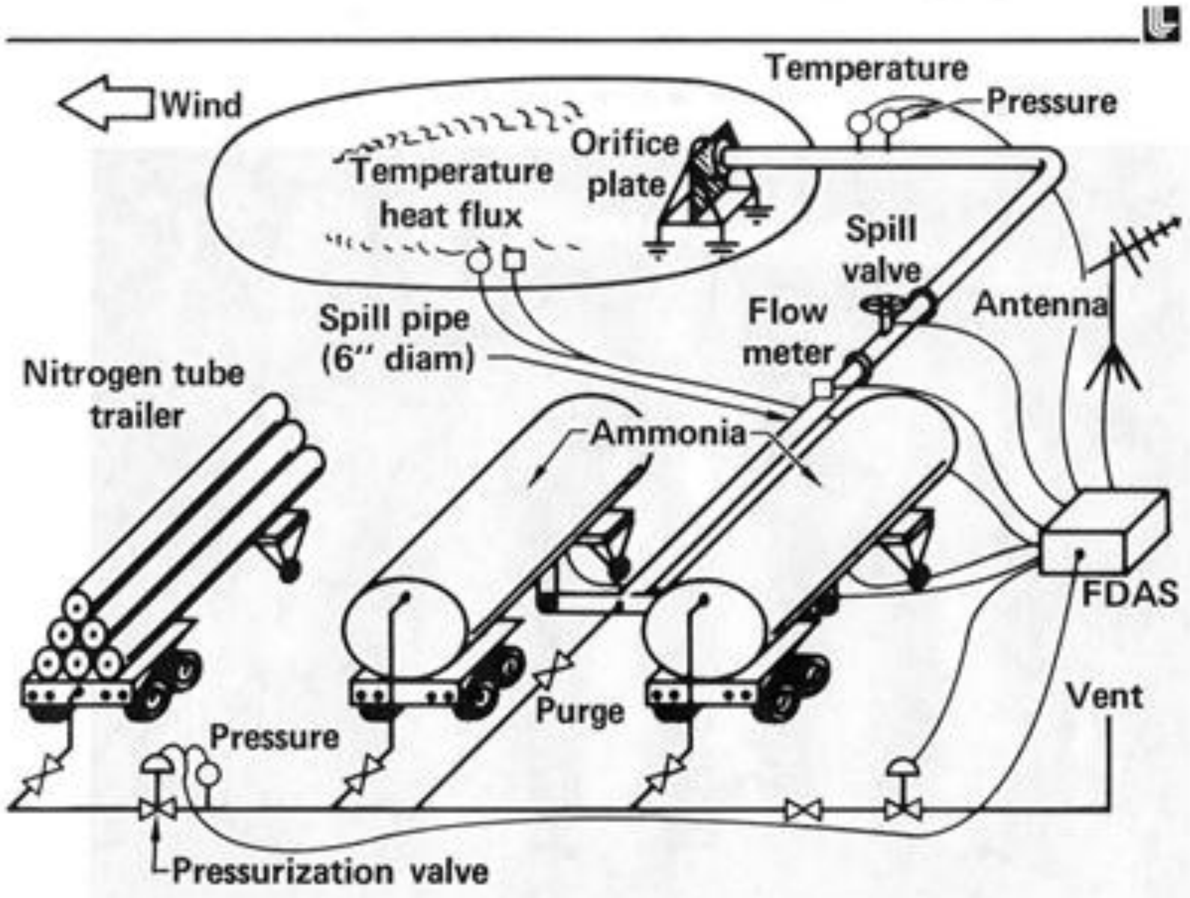


Fig. 1. Temporary ammonia spill facility used for the Desert Tortoise series of experiments at the Nevada Test Site in 1983.

Desert Tortoise Sampling Grid

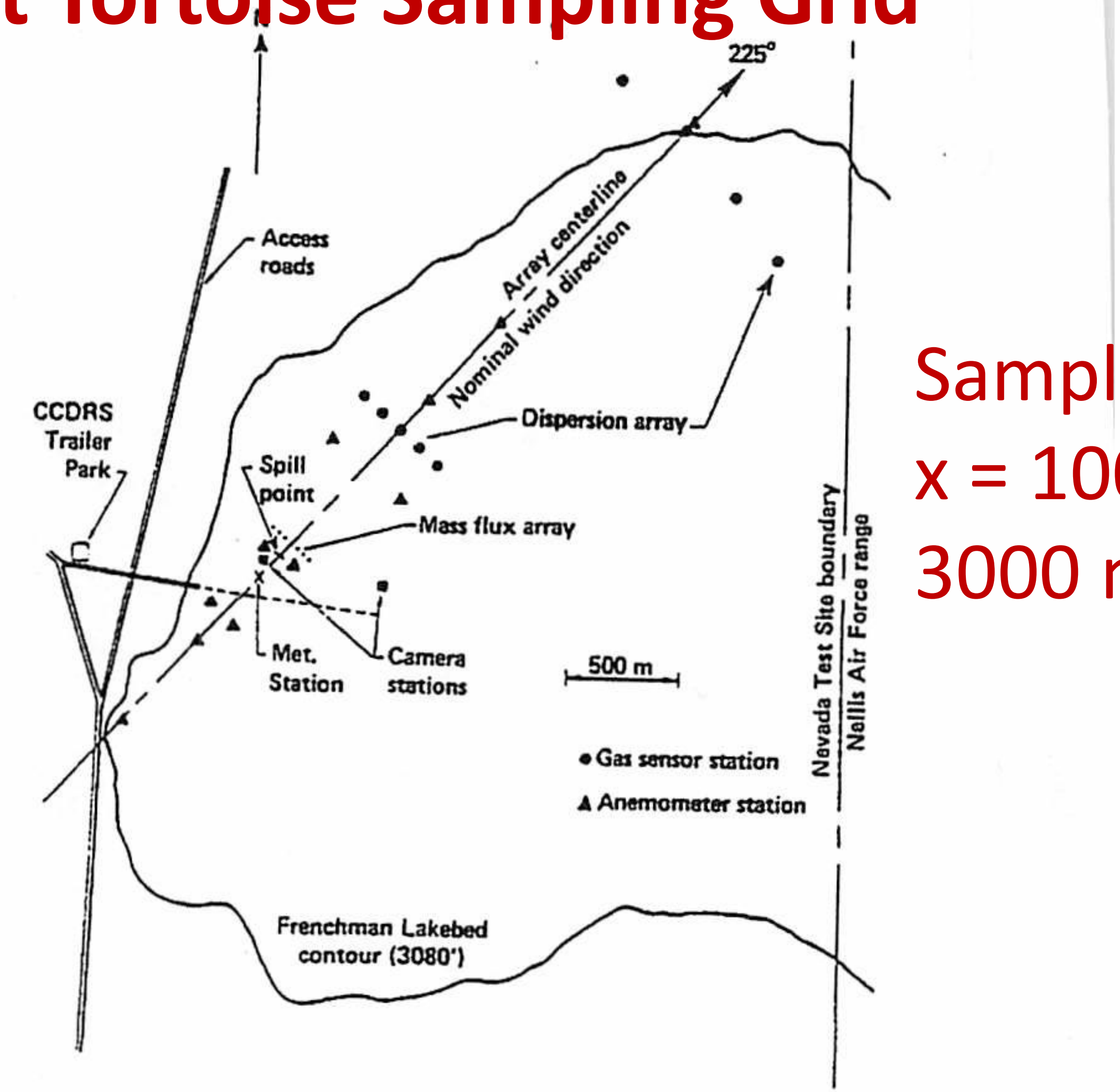
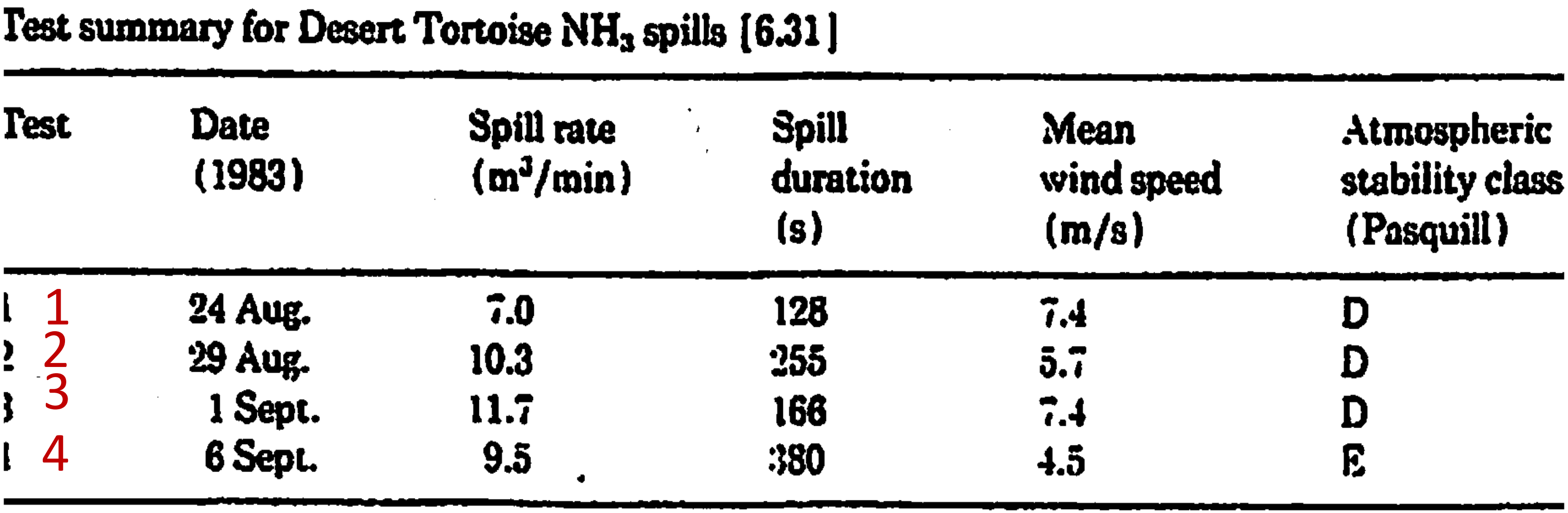


Fig. 1. Diagnostic instrument array for Desert Tortoise and Eagle series experiments [6].

Samplers at x = 100, 800, 3000 m

Characteristics of the four Desert Tortoise two-phase ammonia releases



Test summary for Desert Tortoise NH_3 spills [6.31]

Test	Date (1983)	Spill rate (m^3/min)	Spill duration (s)	Mean wind speed (m/s)	Atmospheric stability class (Pasquill)
1	24 Aug.	7.0	128	7.4	D
2	29 Aug.	10.3	255	5.7	D
3	1 Sept.	11.7	166	7.4	D
4	6 Sept.	9.5	380	4.5	E

Liquid density = 0.68 g/cm^3 or 680 kg/m^3

Desert Tortoise Anhydrous Ammonia Release 2 (Controlled Field Experiment). A two-phase release from a pressurized tank.

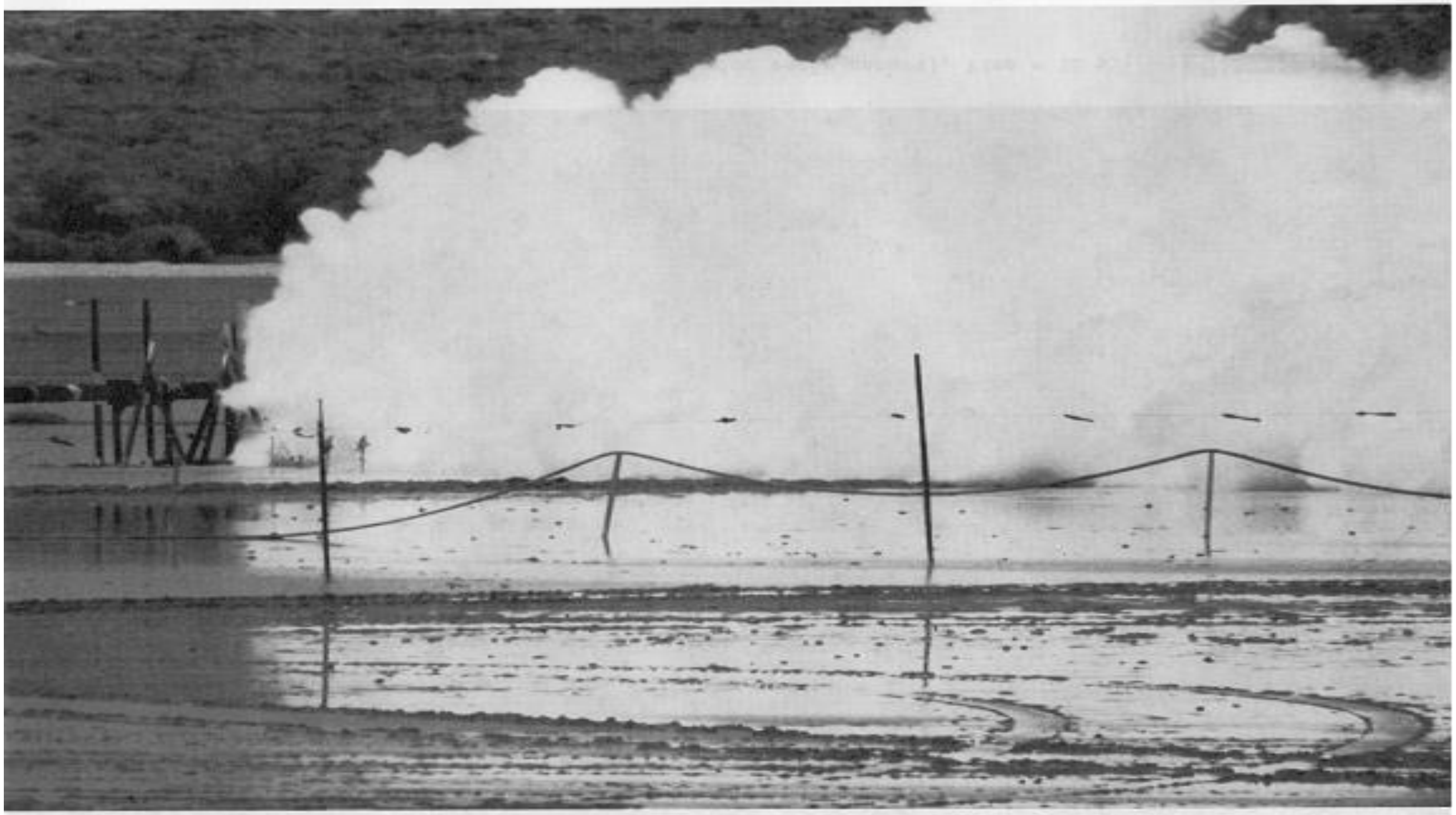


Fig. 18. Desert Tortoise 2 (crosswind narrow angle camera). Time = 35 s.

Lawrence Livermore National Laboratory

DT ammonia release 2 view from distance. Dense behavior is due to embedded aerosols

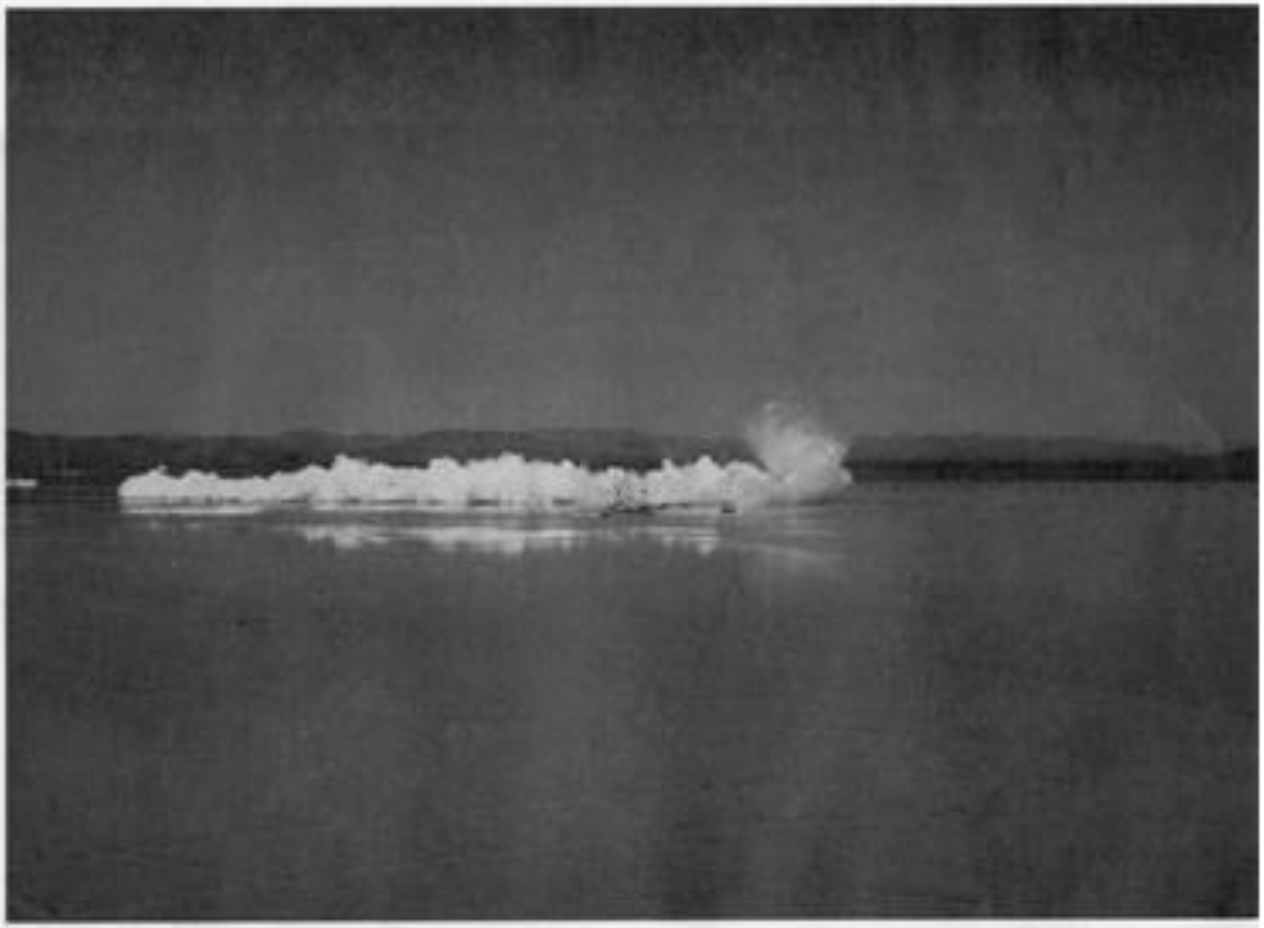


Fig. 17. Desert Tortoise 2 (crosswind wide angle camera). Time = 35 s.

Lawrence Livermore National Laboratory

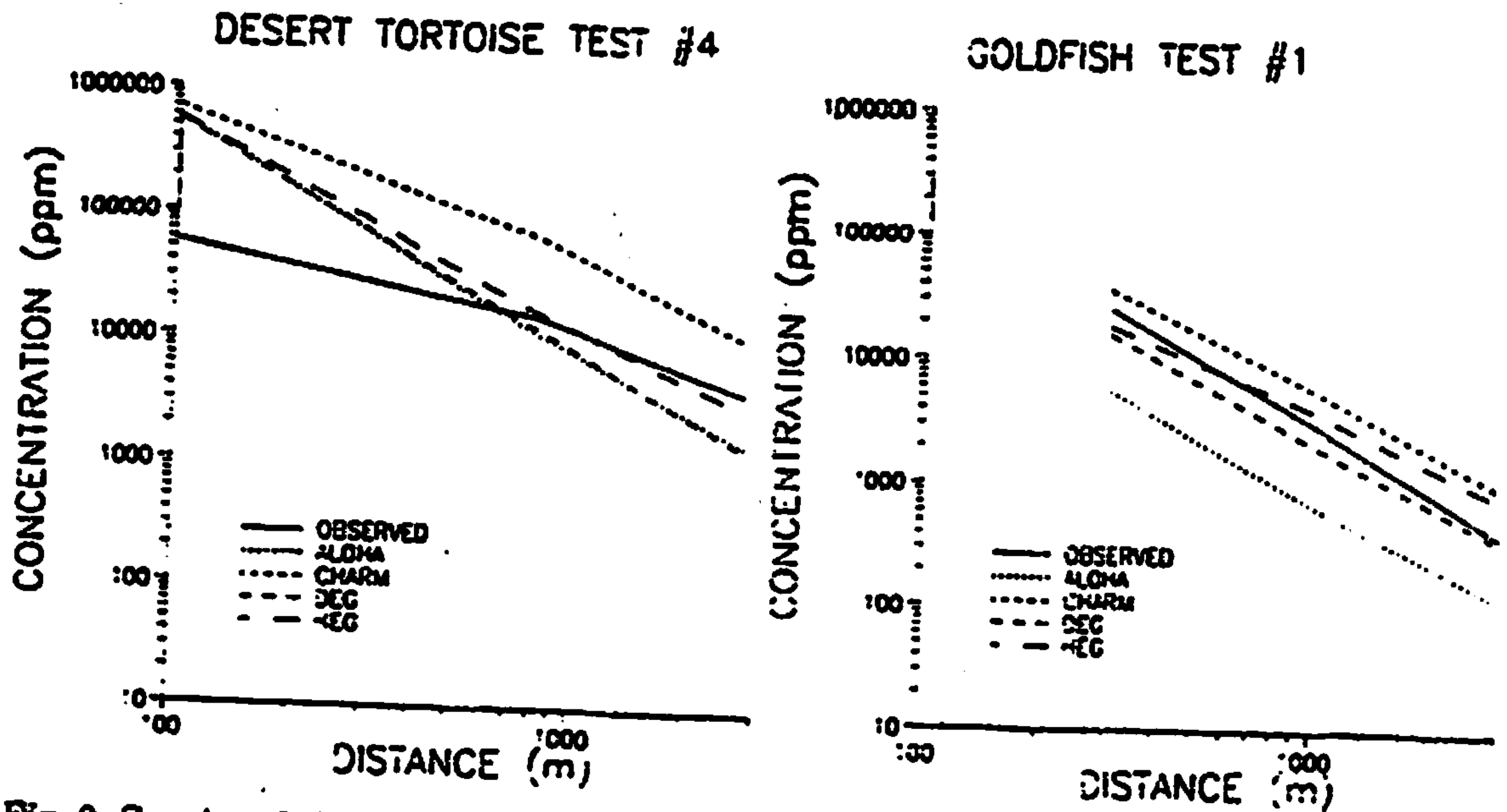


Fig. 2. Graphs of observed and predicted concentrations as a function of downwind distance for Desert Tortoise test 4 (left) and Goldfish test 1 (right). Each figure contains predictions of the ALOHA, CHARM, DEGADIS, and HEGADAS models.

Jack Rabbit I 2010 Field Experiment

- Five releases of pressurized liquefied anhydrous ammonia, of 1 or 2 tons each
- In general the ammonia cloud exhibited dense cloud behavior (due to embedded ammonia liquid aerosols), but not as much as the chlorine cloud. Chlorine has a larger MW

Jack Rabbit I ammonia cloud, 2 sec after release initiation (wind speed 1 m/s)

Jack Rabbit Ammonia Cloud, 1 minute after release starts (wind speed 1 m/s)

Evaporation of liquid pool from refrigerated ammonia spill

- Minimal recent data
- Some liquid spill data from small-scale experiments by Frie et al 1992 used by Leonelli et al 1994. Summarized in Hanna et al 2010 report on DTRA TIC source emissions improvement project
- Apparently the modeling community considers the liquid pool evaporation problem “solved”

Observed and modeled evaporation from small-scale refrigerated liquid ammonia spill (Frie et al. 1992, Leonelli et al 1994)

Best performing model is Mackay and Matsugu 1973

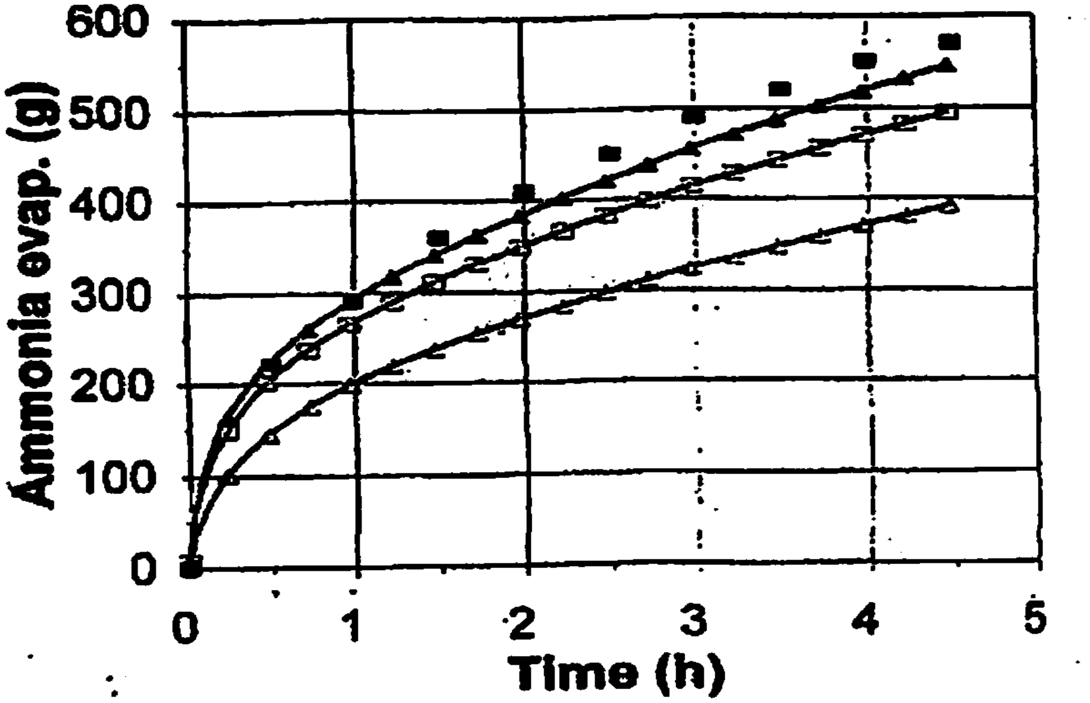


Figure X-4. Comparison of time variation of observed and modeled evaporated mass of ammonia, from Leonelli et al. (1994). The data (solid squares) are from Frie et al. (1992), and the three modeled curves represent three alternate ways for estimating the molar transport coefficients.