Comparisons of Dense Gas Dispersion Models with Field Experiments

There are only a few experiments sponsored by government and private industry where hazardous chemicals are purposely released and the downwind concentrations of the resulting chemical cloud measured. The releases have been done at a safe location such as the HazMat Spill Test Center near Mercury, Nevada, which is operated by the U.S. Department of Energy. Because of the expense in conducting large-scale tests, only a limited number have been done, and even fewer test results are in the public domain. Various researchers have compared the results with models predicting chemical cloud dispersion.

This article examines large releases of anhydrous ammonia and anhydrous hydrofluoric acid at the HazMat Spill Test Center under controlled conditions and compares concentrations measured downwind with those predicted using ALOHA, the SLAB model, and the PEAC tool.

Anhydrous Hydrofluoric Acid Spill Experiments

During the summer of 1986, the Amoco Oil Company and Lawrence Livermore National Laboratory conducted a series of six anhydrous hydrofluoric acid releases called the "Goldfish Test Series" at the HazMat Spill Test Center, then known as the Department of Energy Liquified Gaseous Fuels Spill Test Facility. The results were presented in a paper by D.N. Blewitt, J.F. Yohn, E.P. Koopman, and T.C. Brown at the International Conference on Vapor Cloud Modeling at Boston, MA, on November 2-4, 1987. The U.S. Environmental Protection Agency later compared the results with two dense gas dispersion models (DEGADIS and SLAB) in the public domain, presenting their findings in a paper (J.S. Touma et al, "Performance of Dense Gas Dispersion Models", Journal of Applied Meteorology, 34(3), 603-615, 1995. Other researchers, notably Steve Hanna of Sigma Research Corporation in Concord MA, also compared the Goldfish Test Series results to various model predictions (see reference cited at end of this newsletter). This set of tests is one of very few releasing toxic chemicals under controlled conditions in existence.

One of the objectives of the tests conducted by the sponsors was to evaluate a method of using water spray to knock down the hydrofluoric acid toxic gas cloud resulting from a spill in addition to providing a check for dense gas dispersion models. Therefore three tests were done using water spray and three tests were done without water spray. Since our objective is to look at gas dispersion and not compare the effectiveness of water spray, we will look at the first three tests only. As the Goldfish test series results were made public, modelers examined how the test results compared with model predictions.

The experimental setup consisted of a 5000 gallon capacity horizontal trailer tank modified to accommodate a 4-inch diameter spill line fitted at the end with an orifice. The tank itself was pressurized with gaseous nitrogen and controlled to maintain a constant discharge rate during a test. A load cell located at the hydrogen fluoride trailer provided a continuous record of the trailer weight, from which the hydrogen fluoride discharge rate could be calculated. The discharge pipe was also equipped with a remote controlled spill valve to initiate and terminate the spill. The hydrogen fluoride tank was also equipped with electrical heaters capable of heating the tank to 40°C. Arrays of sensors were placed at different elevations on arcs 300 meters, 1000 meters, and 3000 meters downwind at a dry lake bed known as Frenchman Flat. A characteristic of the site was that the winds typically blow in a predictable direction (about 225° azimuth) which simplified placement of sensors on the arcs. Two different analytical methods were used for the hydrogen fluoride sensors, one method had a sampling time ranging from 67 to 100 seconds depending upon location [total of 62 sensors], and the other method had a sampling time between 10 and 45 seconds depending upon location [total of about 30 analyzers]. Additional details are available in the Blewitt paper describing the tests, cited earlier.

Six anhydrous release tests were completed. The first three tests involved straight anhydrous hydrogen fluoride releases. The last three tests also involved injecting a water spray just upwind to demonstrate a method of hydrogen fluoride plume control. We will look at the first three tests only which are summarized in table 1.

Table 1 Anhydrous Hydrogen Fluoride "Goldfish Test Series" Summary

Test	Spill Rate, gal/min	HF Tank Temp, °C	HF Tank Pressure, psig	Duration, sec.	Wind, m/s @ 2 m	Centerline Concentration, ppm, at 300 m	1000 m	3000 m
1	469.2	40	111	125	5.6	25,473	3098	411
2	175.1	38	115	360	4.2	19,396	2392	*
3	171.6	39	117	360	5.4	18,596	2492	224

*inoperative sensors near cloud centerline at 3000 meters, test 2.

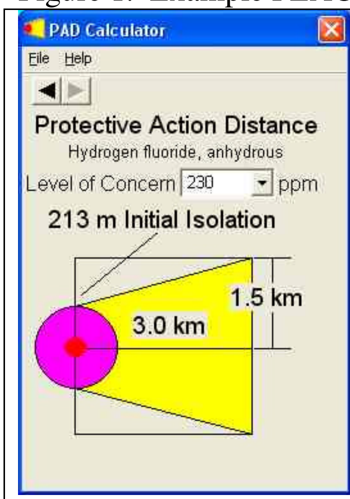
The normal boiling point temperature of hydrogen fluoride is about 20°C. But the hydrogen fluoride was heated to about 40°C (104°F) in the tank under pressure. Thermodynamic calculations estimate that about 14% of the hydrogen fluoride should flash as a gas as it leaves the discharge pipe (the rest being a liquid). But the discharge setup was such that the hydrogen fluoride left the orifice with enough kinetic energy that the liquid portion formed an aerosol rather than dropping to the ground as a liquid. The aerosol remained entrained in the gaseous cloud as it traveled downwind. As the aerosol evaporated, it chilled the cloud, and the cloud behaved as a dense gas at least closer to the source. For modeling purposes, the spill rate was set equal to the discharge rate (source rate). The meteorological conditions correspond to a "D" atmospheric stability.

The density of liquid hydrogen fluoride is approximately the same as water. To convert the spill rate in gallons per minute to kilograms per second, multiply by 3.781/60 = 0.0631, [1 gallon = 3.871 liters, 1 liter water = 1 kilogram], or the test 1, 2, and 3 release rate is 29.2, 11.05, and 10.82 kg/s respectively. We have enough information to model the release using the PEAC tool, the SLAB model, and ALOHA (version 5.4.1).

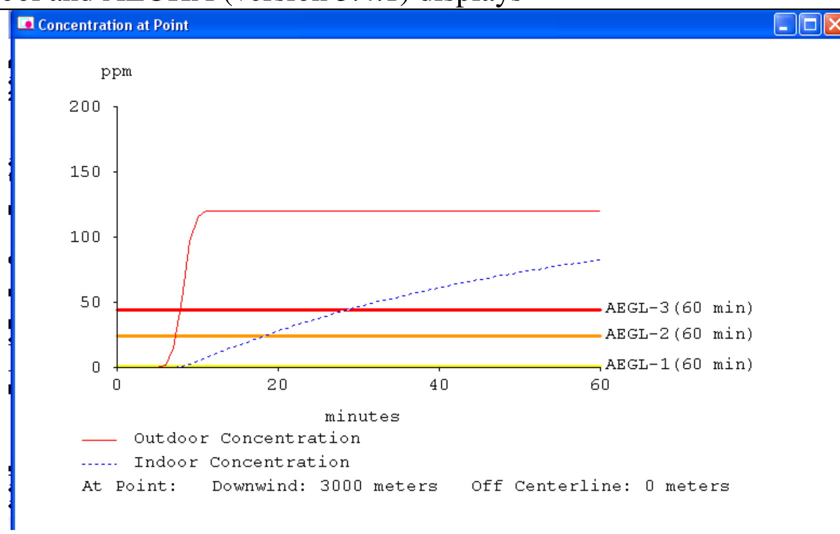
Table 2. Comparison of Model Predictions (Concentrations in parts per million, ppm) with Goldfish Test Results at 300, 1000, and 3000 meters

Test	Actual			ALOHA			SLAB			PEAC tool		
	300	1000	3000	300	1000	3000	300	1000	3000	300	1000	3000
1	25473	3098	411	5500	680	125	7650	960	139	8300	1200	230
2	19396	2392	No data	2850	340		4349	516	70.4	5200	770	
3	18596	2492	224	2100	260	46	3143	365	66	3400	500	90

Figure 1. Example PEAC tool and ALOHA (version 5.4.1) displays



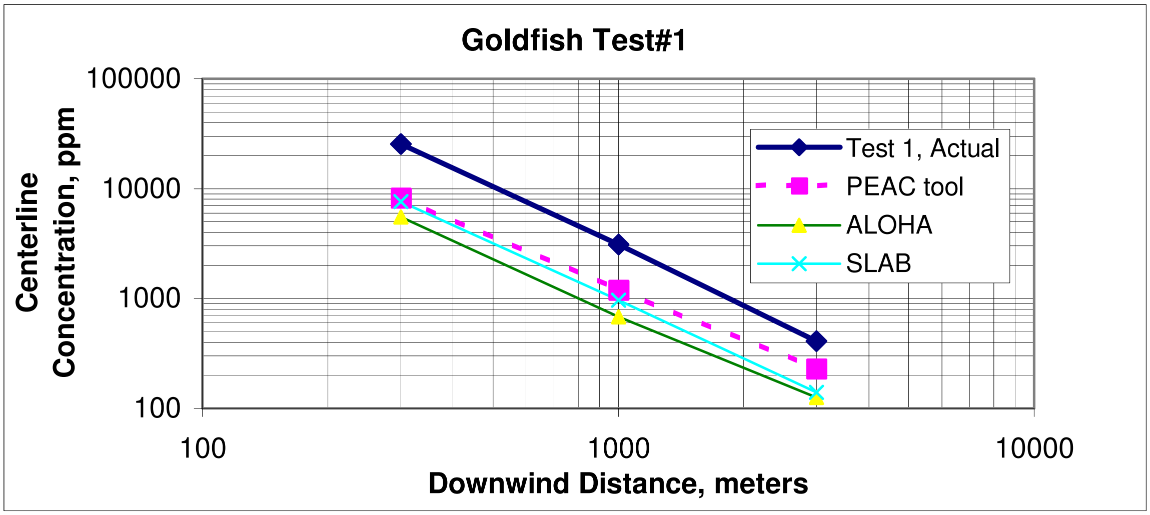
PEAC tool display, test 1, Protective action distance at 3000 m matches 230 ppm level of concern, the display format follows the Emergency Response Guidebook.



ALOHA display, test 1, user input at 3000 meters, display (outdoor concentration graphed, ignore indoor concentration) 125 ppm concentration, AEGL levels also displayed for a 60 minute exposure time, modeled as a continuous release

All of the models as used in this example underpredicted concentrations compared to what was measured in the Goldfish series tests. This was also noted at the time the tests were done when test results were compared with other gas dispersion models available during the late 1980's. The rational given by Amoco Oil Company (one of the test sponsors) and other reviewers was that the liquid instead of pooling near the pipe/orifice exit (a catch basin was provided) formed a fine aerosol which remained entrained in the gas. The aerosol formation was the result of the unusual setup for the test. As the aerosol evaporated, it extracted heat from the surroundings. The result was a chilled dense-gas vapor cloud that rolled downwind on the ground. Neither the ALOHA model nor the PEAC tool has the capability for the user to adjust parameters for this type of behavior. Both the SLAB model and the PEAC tool used a surface roughness of z_o = 0.001 meters, which is discussed further in the next paragraph.

Figure 2. Graph of Goldfish Test Number 1 Comparisons with Models



Steve Hanna of Sigma Research Corporation in a 1993 paper [S.R. Hanna et al, "Hazardous Gas Model Evaluation with Field Observations" Atmospheric Environment 27A pp. 2265-2285 (1993)] also noted that the SLAB model and the DEGADIS model (the DEGADIS model is used in ALOHA versions, dense gas calculations) as well as several other models also underpredicted what was observed in the Goldfish series tests. However, the authors (Hanna et. al) mention if the molecular weight in the DEGADIS model is "tweaked" to represent an aerosol-gas mixture, the DEGADIS model predicts greater concentrations near the source. The SLAB model was developed by Lawrence Livermore National Laboratories (one of the sponsors of the Goldfish Test series), and in 1990, the SLAB model incorporated a horizontal jet release source where the user could incorporate the fraction of liquid aerosol. The authors also pointed out that the Goldfish test series was carried out on a flat, smooth dry lake bed with an estimated surface roughness of only $z_o = 0.0002$ meters. By comparison the default ALOHA surface roughness for a flat surface is 0.003 meters. The default surface roughness for the PEAC tool flat surface is $z_o = 0.001$ meters. This sounds like a lot of mumble-jumble to responders, but the authors did present a table in their paper (table 3) showing modeling results closer to what was observed especially when modeled at $z_o = 0.0003$ meters.

Table 3. Comparison of Model Concentration (ppm) Results presented in the Hanna 1993 Paper with Goldfish Series Test Results

Test	**Actual**			**DEGADIS (z_o = 0.003 m)**			**DEGADIS (z_o = 0.0002 m)**			**SLAB (z_o = 0.003 m)**			**SLAB (z_o = 0.0002 m)**		
	300m	1000m	3000m	300m	1000m	3000m	300m	1000m	3000m	300m	1000m	3000m	300m	1000m	3000m
1	25473	3098	411	16270	2222	397	33116	3801	599	13020	1678	208	20688	2580	319
2	19396	2392	No data	8126	1132		16530	1928		6208	811		9819	1223	
3	18596	2492	224	7260	1077	130	13540	1732	223	6808	942	152	10854	1509	243

What can we learn from this?

- How a chemical is released greatly affects downwind concentrations especially near the source. The hydrogen fluoride was released as a ground-hugging aerosol, which chilled the toxic cloud as the aerosol evaporated extracting heat from the surroundings. The low toxic cloud spread downwind along the ground resulting in higher concentrations than predicted by the models.
- Surface roughness especially near the source tends to help break up and disperse the ground hugging toxic cloud. The surface at the release site for the Goldfish tests was very smooth.

Both ALOHA and the PEAC tool were developed for use by first responders to be used in real-world accidents. In a real-world situation, anhydrous liquid hydrogen fluoride is more likely to be stored in a tank with a refrigeration system, or with a liquid hydrocarbon cap, and not under conditions mimicking the tests. If an accident occurred, the chemical is more likely to be modeled released all at once as in an explosion or tank fire (worst case scenario), or a liquid pool which evaporates, or as a gaseous vent, all of which can be modeled using ALOHA or the PEAC tool.

Anhydrous Ammonia Spill Experiments

This series of tests, called the "Desert Tortoise" series tests releasing anhydrous liquefied ammonia, is similar to the Goldfish tests using hydrogen fluoride. The tests were conducted in 1983 by Lawrence Livermore National Laboratories at the same site as the Goldfish tests, and are described in a report by Goldwire et al, 1985 [Goldwire, H.C. Jr. et al, "Desert Tortoise series data report 1983 pressurized ammonia spills", UCID-20562, Lawrence Livermore National Laboratories, Livermore, CA]. Pressurized and liquefied anhydrous ammonia stored at ambient temperature was released from a tank via a jet directed horizontally downwind in a series of four tests, the release point one meter from the ground. Because of a rainstorm just prior to the releases, the dry lake bed known as Frenchman Flat was covered by a shallow layer of water during most of the experiments. At the release point, about 18% of the liquid flashed, becoming a gas. The rest of the liquid became entrained as a fine aerosol in the gaseous cloud. Very little unflashed liquid was observed to form a pool on the ground. Ammonia concentrations and temperatures were obtained from towers placed along arcs at distances 100 and 800 meters downwind at heights ranging from 1 to 8.5 meters. In addition, portable ground level stations measured ammonia concentrations at 1400 or 2800 meters, or 3500 and 5600 meters. Like the Goldfish series tests, the Desert Tortoise series test results were made available to gas dispersion modelers.

Table 4 Anhydrous Ammonia “Desert Tortoise Test Series” Summary

Test	Amount Released lbs	Release Rate, lb/min	Wind, m/s @ 2 m height	Stab.	Peak Centerline Concentrations (ppm)* at downwind distances of					
					100m	800m	1400m	2800m	3500m	5600m
1	24500 2 minutes	12250	7.42	D	50000 *49943*	10000 *8843*			650	150
2	66000 4 minutes	16500	5.76	D	80000 *83203*	15000 *15658*	5000			
3	50000 3 minutes	16700	7.38	D	80000 *76881*	12000 *7087*		600		
4	90000 6 minutes	15000	4.51	E	65000 *57300*	17500 *19618*		5000		

*There is some disagreement in the literature on estimation of maximum centerline concentration calculated from sensors. First number is from U.S. EPA Background Document for Offsite Consequence Analysis, published April 1999. Second number (*in italics)* is from S.R. Hanna et al, 1993. A “blank” means no sensor measurements. Figures 3 through 6 averaged the two numbers.

The Desert Tortoise test results can be compared with model predictions. We used the PEAC tool, the ALOHA model (version 4.5.1), and the SLAB model developed by Lawrence Livermore National Laboratories. The SLAB model allows the user the option of releasing the chemical as a horizontal jet downwind for a short period of time mimicking the Desert Tortoise field conditions. Neither the ALOHA or the PEAC tool has that option. The intent of ALOHA and the PEAC tool is to provide quick answers to emergency responders to spill situations likely to be encountered; therefore ALOHA and the PEAC tool provided a simplified list of common possible spill options. The results are graphed on a log-log scale in figures 1, 2, 3, and 4. All models used a surface roughness $z_o = 0.001$ meters.

Figure 3. Desert Tortoise Test Number 1

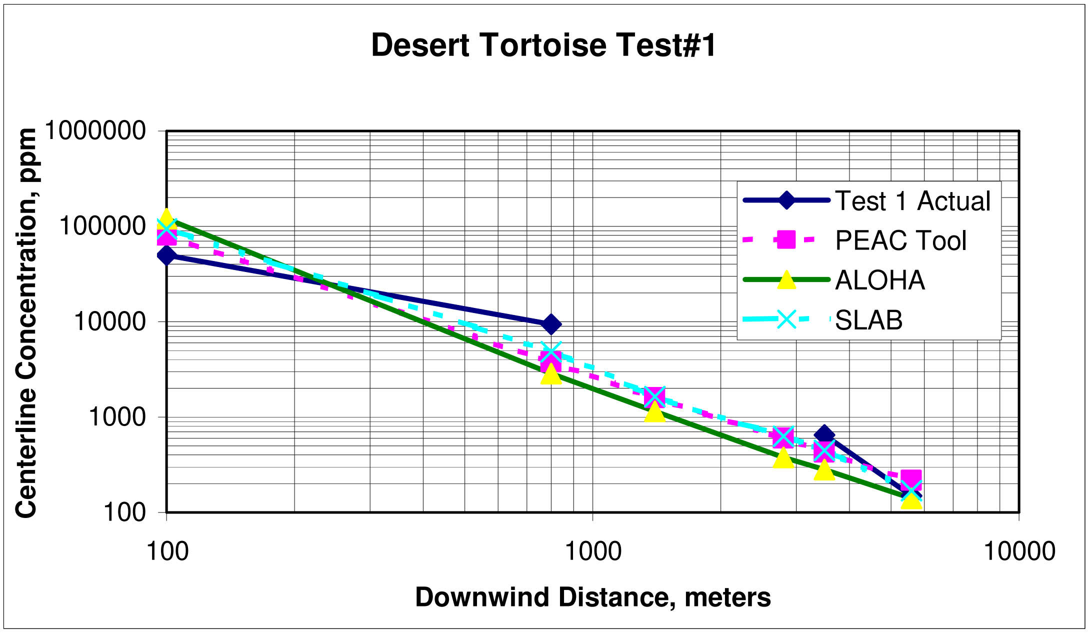


Figure 4. Desert Tortoise Test Number 2

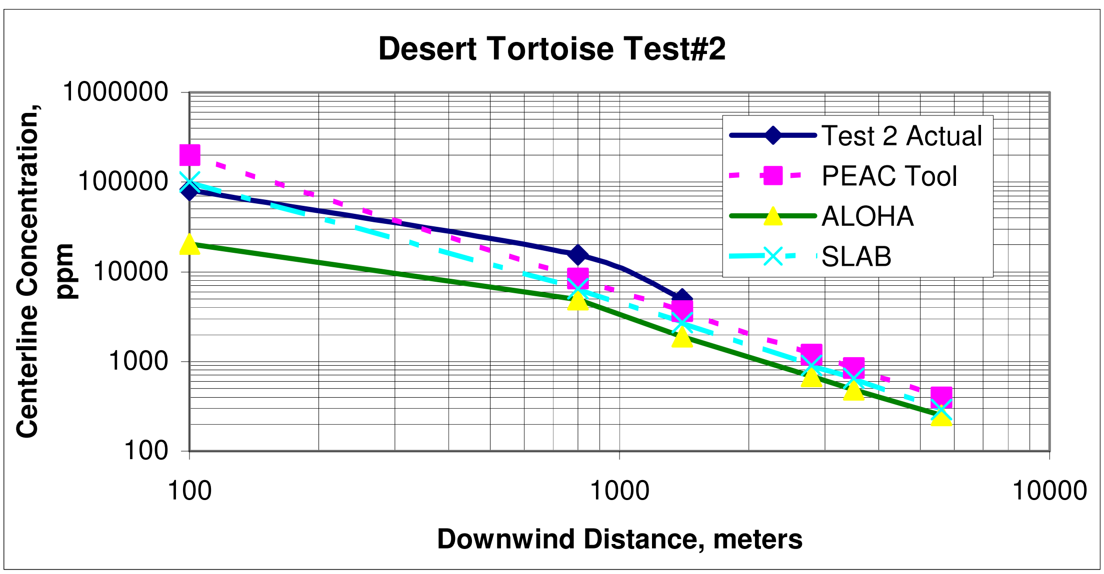


Figure 5. Desert Tortoise Test Number 3

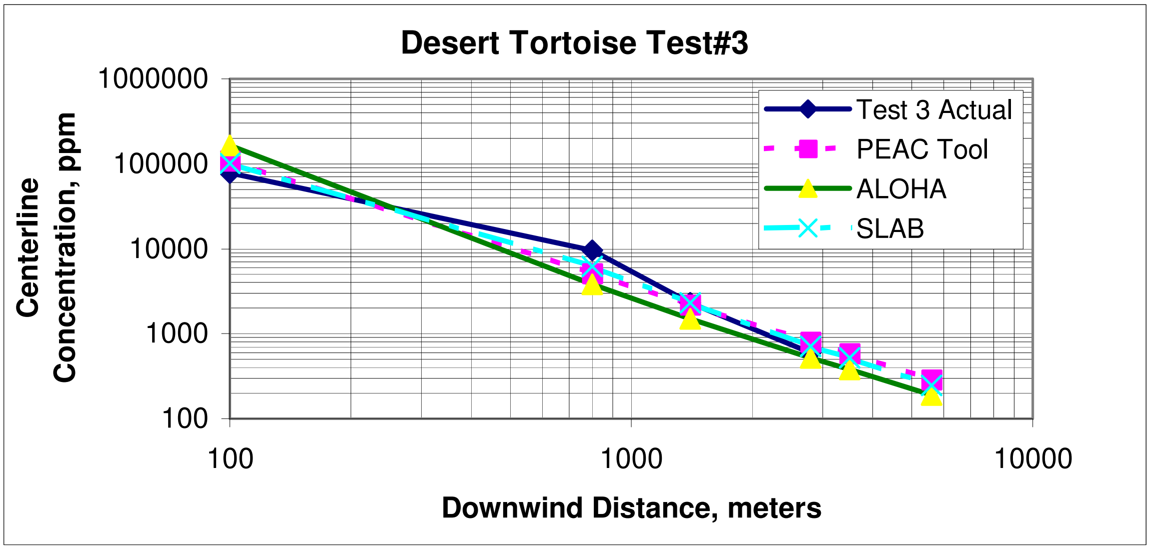
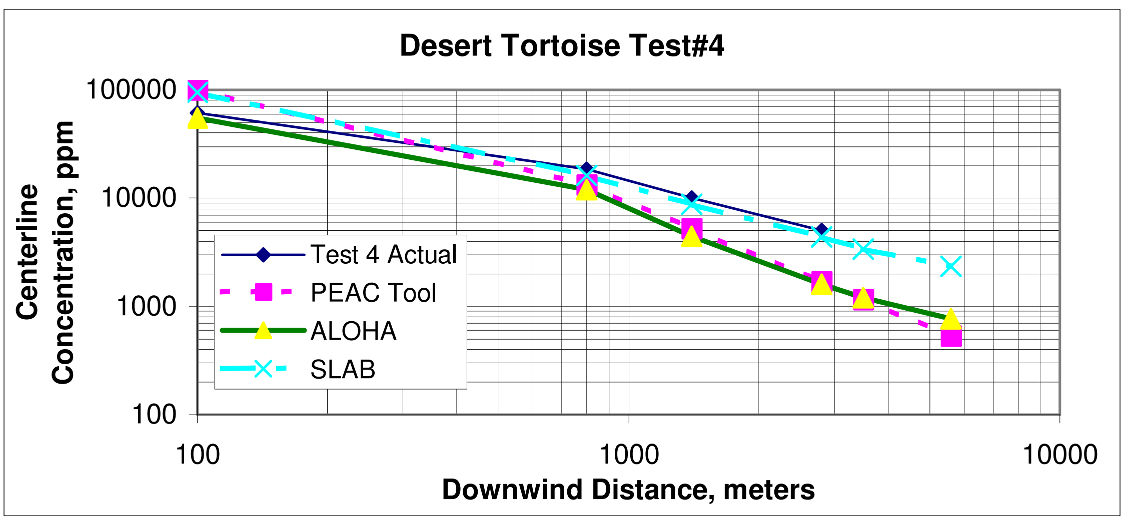


Figure 6. Desert Tortoise Test Number 4



The measured downwind concentrations are in the right ballpark for concentrations predicted by the PEAC tool, ALOHA, and SLAB. The PEAC tool probably had the best agreement for test numbers 1 and 2, but SLAB was closer to measured concentrations for test number 4. All three models were fairly close for test number 4. There was also a lot of scatter in the measured concentration data, which reflects the difficulty of trying to capture the centerline concentration using an array of sensors. Generally, the concentrations estimated from sensors at 100 meters were less than the numbers predicted from models, but concentrations at 800 meters were greater than predicted from models. Unfortunately, there were too few measurements for sensors stationed far from the source to draw definite conclusions, but the limited data available seemed to agree with model predictions.

Modeling Lessons Learned

- Toxic chemical releases are complex, especially those involving large releases of dense gases. A lot of things can happen. There is a need to perform full-scale releases especially of dense gases at a safe location to check out the prediction ability of gas dispersion models.
- The dense gas component of SLAB, ALOHA, and the PEAC tool roughly predicted the dense gas dispersion of the ammonia release but under predicted the hydrogen fluoride release. The modeling was done near ground level (the PEAC tool predicts concentration at a default height of 0.1 meters (10 cm)). The difference was that the experimental setup involved heating the storage tank (37^o to 40^o) under pressure and releasing the chemical through an orifice; the kinetic energy at the release point caused the hydrogen fluoride to be released as a fine aerosol. The resulting toxic cloud behaved as a dense gas hugging the ground, which did not "lift off" at least not at the locations of the sensors. The sensors near the top of the towers did not measure significant hydrogen fluoride (the hydrogen fluoride was near the ground).
- The method of release does affect airborne concentrations closer to the source. The implication for the PEAC tool is that a compromise must be made as to the level of detail to be asked of responders in order to calculate answers. It does no good to ask responders detailed questions that he/she may not know for a real-world spill when a quick answer is needed.

References

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