Technically Speaking
Hydrogen Fluoride - Spilled and Tested.
by Dr. John Nordin

HYDROGEN FLUORIDE:

How well do atmospheric dispersion models predict downwind concentrations?

An Actual Incident.

The date is 30 October 1987. The place is Marathon Corporation refinery at Texas City, Texas. A crane accidentally dropped equipment on top of a pressurized tank containing liquid hydrogen fluoride severing two pipes at the tank top permitting hydrogen fluoride to escape as a gas. The tank was approximately 12 feet in diameter and 20 feet high and had a capacity of 200,000 lbs of hydrogen fluoride. The temperature at the time was in the mid 70's which corresponds to a vapor pressure of hydrogen fluoride somewhere near 840 or 850 mm Hg, or roughly 2 psig inside the tank. The normal boiling point of hydrogen fluoride is 68^{o}F. The hydrogen fluoride liquid had a cap of isobutene designed to reduce the evaporation rate of the hydrogen fluoride. Nevertheless, an estimated 36,000 lbs of hydrogen fluoride evaporated and escaped from the tank during the first hour after the top pipes were sheared plus perhaps another 4000 lbs during the second hour before the tank reached atmospheric pressure and was isolated.

About 3000 people in 52 city blocks were evacuated. The fluoride plume was described as 2 to 3 miles long and 0.5 to 1 mile wide. The wind was from the SE at 5 to 10 mph. Critics (at the Environmental Policy Institute in Washington DC) have stated that 70,000 people should have been evacuated, and the evacuation area should have included a downwind semicircle of 7.5 miles radius. Technical details on effects of community exposure to hydrogen fluoride during the Texas incident has been published in a paper,

Dayal, Hari; Brodwick M; Morris R,;Baranowski T; Trieff N; Harrison J; Lisse J; Ansari G. "A Community-based Epidemiologic Study of Health Sequelae of Exposure to Hydrofluoric Acid (HF)", Annals of Epid. 2, 213-230, 1992.

The accident could have been a lot worse. Had the sheared piping been on the side or bottom of the tank, hydrogen fluoride liquid would have gushed out quickly. There could have been many deaths, according to Dr. Fred Millar of the Environmental Policy Institute who issued a public statement following the accident.

Health Effects from Exposure to Hydrogen Fluoride

The NIOSH Pocket Guide to Chemical Hazards lists worker 8-hour exposure limits to hydrogen fluoride (both NIOSH and OSHA) as 3 ppm, or 2.5 mg/m^3 as fluoride. The IDLH limit is listed as 30 ppm. Anhydrous hydrogen fluoride dissolves in water (including moisture in the air) to produce hydrofluoric acid.

Acute symptoms of exposure to hydrogen fluoride or hydrofluoric acid results in irritation of the eyes, nose, and throat; pulmonary edema (fluid in the lungs); skin and eye burns; nasal congestion, and bronchitis.

Chronic effects of exposure (by inhalation or ingestion) include fluorosis, weight loss, malaise, anemia, leucopenia (low blood leukocyte count), and osteosclerosis (bone abnormality)

The LC50 value represents the lethal concentration in air of a toxic chemical in which 50% of the test animals die due to exposure for a specified period, usually 1 hour. It does not include possible later deaths due to cancer or organ damage rendering the animal susceptible to infection or other problems. The LC50 value (1-hour) for rat inhalation is 1278 ppm; for mouse inhalation (1-hour) is 500 ppm.

Repeated inhalation of 17 ppm hydrogen fluoride in guinea pigs and rabbits resulted in damage to the lungs, liver, and kidneys of these test animals; a similar test at 8.6 ppm failed to show organ damage. Another sub-lethal test of prolonged inhalation doseages at 25 mg/m^3 (30 ppm) resulted in hemorrhage and edema of the lung (dog, rabbit, and rat test animals).

The American Industrial Hygiene Association has developed Emergency Response Planning Guidelines for Hydrogen Fluoride as well as other chemicals. Their Level 2 Guideline (ERPG-2) has been accepted by many emergency responders for evacuation purpose. The ERPG-2 guideline for hydrogen fluoride is 20 pmm and is defined as the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. When running an atmospheric dispersion model to a Level of Concern for evacuation purposes, the ERPG-2 is usually selected as that level of concern.

Occasionally a more conservative number, ERPG-1 is selected. ERPG-1 for hydrogen fluoride is 2 ppm and is defined as the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor.

Amoco Corporation Tests in Nevada

Hydrogen fluoride is used by some refineries in a step for the manufacture of unleaded gasoline. Because no one knew for sure how liquid hydrogen fluoride would behave in a spill, the Amoco Corporation arranged with the Department of Energy to spill 1000 gallons in two tests at the HazMat Spill Center (formally called the National Spill Test Facility) near Mercury, Nevada. This series of gas dispersion experiments are known as the Goldfish test series. Conventional wisdom at the time suggested that the hydrogen fluoride would spill on the ground as a liquid with some gas, and the liquid would evaporate over some period of time. Two spills were completed on 1 August and 6 August 1986: (1) 1000 gallons in 2.05 minutes [Goldfish-1] and (2) 1000 gallons in 6 minutes [Goldfish-2]. No liquid pool was formed. Instead a ground hugging mist formed, containing initially 20% gas and 80% aerosol which was quickly carried away in the wind. Three arrays of fluoride measuring sensors were located downwind to measure the concentrations in the air.

A total of six experiments were completed in 1986, which included three more tests [Goldfish-4, 5, and 6] demonstrating the effectiveness of water spray in knocking down hydrogen fluoride mist and gas plus a repeat of the 6 August test under a higher dewpoint condition [Goldfish-3]. All six tests resulted in a ground-hugging mist consisting of 80% aerosol and 20% gas. Details are published by D. Blewitt, J. Yohn, R. Koopman, and T.C. Brown, 1987, "Conduct of Anhydrous Hydrofluoric Acid". International Conference on Vapor Cloud Modeling, Boston MA, Nov 2-4, 1987. The water spray test results are described in another paper by the same authors, D. Blewitt, J. Yohn, R. Koopman, T.C. Brown, 1987, "Effectiveness of Water Sprays on Mitigation of Anhydrous Hydrofluoric Acid Releases', Center for Chemical Process Safety.

How Well Do Gas Dispersion Models Predict Downwind Concentration of Hydrogen Fluoride?

Modeling of hydrogen fluoride spills is tricky. Without actual experimental tests, it is difficult to predict what will happen. What gas dispersion model should be used? Most modelers would have guessed that the hydrogen fluoride would form a liquid pool that would quickly evaporate, and the pool would become chilled as the chemical evaporates. After all, this is what happens if chlorine or anhydrous ammonia liquids are spilled. But that is not what happened. As a result all of the popular gas dispersion models (Gaussian, SLAB, ALOHA, etc.) available at that time seriously under predicted downwind air concentrations of hydrogen fluoride when compared with what was actually measured by sensors placed downwind in the Goldfish Series Tests.

The model comparisons with Goldfish Test Results are in a paper, Hanna, S.R., D.G. Strimaites, and J.C. Chang. 1991. "Evaluation of Fourteen Hazardous Gas Models with Ammonia and Hydrogen Fluoride Field Data" Journal of Hazardous Materials 26 pp. 127-158. Ammonia represents another series of tests. None of the models considered a ground-hugging hydrogen fluoride aerosol, and therefore under predicted downwind concentrations.

How Does the PEAC Tool Compare with the Goldfish Test Results?

We will set up the PEAC tool in the flat terrain mode and use metric units. The wind speed is the same as during the Goldfish tests. Skies are clear. We will set the time and date for the Mercury, Nevada location [Las Vegas NV will do]. Like other popular gas dispersion models such as ALOHA, the PEAC tool does not consider ground-hugging aerosols in its model formulation. We will not use the liquid pool option because we know from the Goldfish tests that no liquid pool is formed. There is some question of whether this is a continuous release or a sudden pressure "instantaneous" release so we will run the PEAC tool in both modes. The pertinent information from the Goldfish Tests is listed in Table 1.

Table 1. Summary of Goldfish Hydrogen Fluoride Test Results

Test	Goldfish-1	Goldfish-2	Goldfish-3
Spill rate, gpm	469.2	175.1	171.6
Spill rate, kg/sec	29.5	11.0	10.8
Total Released, kg	3688	3960	3888
Release duration, sec	125	360	360
Wind speed @ 2 m height, m/s	5.6	4.2	5.4
Atmospheric Stability	D	D	D
Field Conc at 300 m, ppm	25,473	19,396	18,596
Field Conc at 1000 m, ppm	3,098	2,392	2,492
Field Conc at 3000 m, ppm	411	no data	224

The field concentrations are near ground level concentrations as measured by sensors. The wind direction at the test site is very predictable so sensors can be located near the expected centerline of the toxic cloud as it travels downwind. There is some interpolation between sensors in order to arrive at Table 1 as it is difficult to locate the sensors at the exact centerline.

When using the PEAC tool in this exercise, we will use the measured field concentrations as the "Level of Concern". We will use either the total mass released (in the instantaneous or "BLEVE" mode) or "mass/sec" in the continuous mode. If the PEAC-calculated distance is less than the Goldfish array distance, then the PEAC tool has underestimated the downwind concentration. If the PEAC-calculated distance is greater than the Goldfish array distance, then the PEAC tool has overestimated the downwind concentrations.

Table 2. Comparison of Goldfish HF Test Results to PEAC® tool Predictions for Continuous Release

Test	Goldfish-1	Goldfish-2	Goldfish-3
Spill rate, kg/s	29.5	11.0	10.8
Release duration, s	125	360	360
Wind speed @ 2 m, m/s	5.6	4.2	5.4
Field C at 300 m, ppm	25473	19396	18596
Field C at 1000 m, ppm	3098	2392	2492
Field C at 3000 m, ppm	411	no data	224
PEAC predicted distance for C at 300-m array, meters	137	107	107
PEAC predicted distance for C at 1000-m array, meters	443	351	290
PEAC predicted distance for C at 3000-m array, meters	1500	-	1200

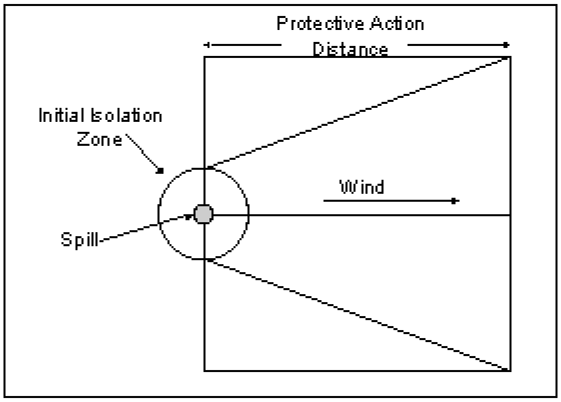
Table 3. Comparison of Goldfish HF Test Results to PEAC tool Predictions for Instantaneous Release

Test	Goldfish-1	Goldfish-2	Goldfish-3
Release duration, s	125	360	360
Amount Released, kg	3687	3960	3888
Wind speed @ 2 m, m/s	5.6	4.2	5.4
Field C at 300 m, ppm	25473	19396	18596
Field C at 1000 m, ppm	3098	2392	2492
Field C at 3000 m, ppm	411	no data	224
PEAC predicted distance for C at 300-m array, meters	839	961	961
PEAC predicted distance for C at 1000-m array, meters	1900	2200	2200
PEAC predicted distance for C at 3000-m array, meters	4400	-	5700

The PEAC tool when operated in the continuous released mode under predicts downwind concentrations of hydrogen fluoride but over predicts downwind concentrations when the BLEVE or sudden pressure release mode is selected. The actual release time for the Goldfish tests were 125 and 360 seconds so there is some debate as to whether this is a continuous release or an instantaneous release. The BLEVE or sudden pressure release is a “worst case” situation when using the PEAC tool.

The PEAC tool was also designed for lower concentrations further downwind from the source, not close up as when trying to compare with the Goldfish tests. Both Tables 2 and 3 indicate that the percentage difference between the PEAC model prediction and the Goldfish tests become less the further downwind. The PEAC tool is intended for predicting protective action distances for much lower concentrations such as for the IDLH value of 30 ppm, and not for very high concentrations close to the source.

Emergency Response Guidebooks



The 2004 Emergency Response Guidebook under hydrogen fluoride (anhydrous), large spills, still recommends an initial isolation zone of 210 meters and a protective action distance (PAD) of 1.9 km (1.2 miles) if a daytime spill or 4.3 km (2 miles) if a nighttime spill. The Goldfish test results indicate that the PAD should be much greater. The concentration at 1.9 km (daytime spill) for a spill equivalent to the Goldfish tests is predicted to be in the ballpark of 500 ppm. The 500 ppm concentration is way above the IDLH value of 30 ppm and approaches the LC50 concentration for some test animals. Dr. Fred Millar of the Environmental Policy Institute in Washington DC also issued a statement following the Marathon Corp. refinery incident saying that the Emergency Response Guidebook PAD for evacuation was too low, and the PAD should be 7.5 miles.

The reason for the relatively low PAD displayed in the Emergency Response Guidebook (ERG) is that the ERG deals with transportation accidents, and “large” is generally taken to mean “greater than 55 gallons” or “many small packages”. Large tanks such as size of the tank containing hydrogen fluoride at Marathon refinery are not shipped. The PADs in the ERG were based on mix of different hypothetical accident scenarios and meteorology and container sizes, and is at a “90 percentile basis”, meaning, that 90% of the cases examined had PADs equal to or less than the ERG listed value. The Level of Concern for the ERG is the Emergency Response Planning Guideline Level 2 (ERPG-2) of 20 ppm. Obviously, the 500 ppm at 1.2 miles is much greater than 20 ppm in case of the Goldfish tests.

The container size or leak rate is critical to the modeling. If responders are not sure of the leak rate, the most conservative approach is to assume that the entire chemical is released at once for the purpose of estimating a PAD.