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Modelling Absorption and Dilution of Unconfined Releases of Hazardous Gases by Water Curtains or Monitors

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ABSTRACT

OSHA Process Safety Management guidelines suggest that a facility operator investigate and document a plan for installing systems to detect, contain, or mitigate accidental releases if such systems are not already in place. In addition, proposed EPA 112(r) regulations would require such analysis. This paper illustrates how mathematical modelling can aid such an evaluation and describes some recent enhancements of the HGSPRAY model: 1) Adding algorithms for modeling NH_3 and LNG mitigation; 2) Modeling spraying of releases with fire water monitors encircling the point of release; 3) Combining wind tunnel modeling with mathematical modeling; and 4) Linking HGSPRAY and HEGADAS. Case cases are presented as examples of how HGSPRAY can aid the design of water spray systems for mitigation of toxic gases (e.g., HF, NH_3) or dilution/dispersion of flammable vapors (e.g., LNG).

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1. INTRODUCTION

The capability of water sprays in mitigating clouds of hydrofluoric acid has been demonstrated in the large-scale field experiments Goldfish and Hawk which took place in the Nevada desert (Blewitt et al, 1987; Schatz et al, 1989). The effectiveness of water sprays and fire water monitors to remove HF from a vapor plume, has also been studied theoretically using the model HFSPRAY, developed by V.M. Fthenakis with support from the Industry Cooperative HF Mitigation Program (ICHMAP) and Amoco Oil Company. HFSPRAY is a two-dimensional spray model that describes absorption of gases by water sprays, air entrainment and heat transfer. It is a complete model of mass, momentum, and heat transfer between air/HF and drops injected by water sprays or monitors. It has been verified against the Hawk field tests performed in the DOE Nevada test site as part of the ICHMAP: HFSPRAY model predictions are within ±6% of the experimental results obtained in the Hawk field tests (Fthenakis, 1989; Fthenakis and Zakkay, 1990, Fthenakis et al 1991). In addition, the model replicated the dispersion patterns observed from boundary layer wind tunnel modeling of water spray mitigation systems from actual industrial installations (Fthenakis and Blewitt, 1993).

HGSPRAY can be linked with the HGSYSTEM models (Puttock et al., 1990) which describe the physical transformations and the dispersion of a jet or plume upstream and downstream of the water spraying region. The HGSYSTEM models describe all the phases of an accidental gaseous release, including depressurization, phase-change, and atmospheric dispersion of buoyant or denser-than-air gases. The HGSPRAY model has been independently verified with experimental data involving releases of HF. The HGSYSTEM models have also been

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independently verified by comparisons with a wide range of experimental databases.

This paper describes some recent enhancements in the HGSPRAY model -which constitute the new version HGSPRAY5- and its application in modeling HF, NH_3 and LNG mitigation systems.

2. EXTENSION OF HGSPRAY TO AMMONIA RELEASES

HGSPRAY is a general model which can simulate the scrubbing of any gas with water sprays, once the gas physical and transport parameters are known. The model describes the gas-phase as a continuous fluid with properties that change with distance in a two-dimensional rectangular grid (Fthenakis, 1993). The characteristics of an ammonia plume (e.g., density, viscosity, diffusivity, concentration, temperature) are a user input to the model. The liquid phase is modeled by considering a finite number of drops of varying size and trajectory. As drops transverse the computational flow field they accelerate or decelerate, evaporate or condense, conduct heat or convect enthalpy and absorb ammonia. Such absorption is controlled by the concentration difference between gas and liquid phases and a gas-phase based overall mass transfer coefficient. This coefficient depends on the Henry law coefficient which can be described as a function of temperature in the drop (Dasgupta and Dong, 1986);

$$\ln H = 4092\, T^{-1} - 9.7$$

The drop temperature is derived from the solution of the energy equation

$$m_k c_p \frac{dT}{dt} = Nu\, k\, \pi\, d(T_g - T) - m_w h_w - m_a h_a$$

where m_k is the mass of a drop k, representing a specific drop size and trajectory, m_w is the drop's evaporation rate, m_a is the rate of NH_3 absorption in the drop, T is the drop temperature, T_g the temperature of the surrounding gas, k the thermal conductivity and c_p the specific heat of water, h_w is the latent heat for water evaporation and h_a is the heat of solution of $NH_3(g) + H_2O$ mixing.

A series of simulations were conducted to predict the effectiveness of water sprays in mitigating ammonia releases from high pressure containers. Release scenarios resembling the Hawk HF tests were chosen to compare ammonia removal with the HF mitigation because the later has been established both in the field and by earlier simulations (Fthenakis et al, 1991). A comparison of NH_3 and HF removal effectiveness as a function of water-to-gas weight ratio, is shown in Figure 1; the corresponding initial conditions are given in Table 1.

The effectiveness of ammonia mitigation will depend, besides the water-to-gas ratio, on several other parameters (e.g., location of release, concentration of ammonia in the plume, positioning of spray nozzles, drop size, wind speed, ambient temperature) in the same way that HF removal is affected by these parameters. Such effects are discussed elsewhere (Fthenakis et al., 1991).

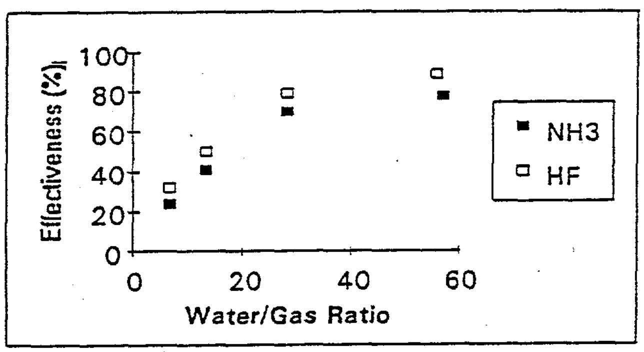

Figure 1. Comparison of Model Estimates of HF and NH_3 Mitigation (Based on the Hawk Test Scenarios)

Table 1. Input Data for HF and NH_3 Simulations

H_2O/ Gas Ratio [1]	Water Flow Rate (kg/s)	Nozzle Type[2]	Water Pressure (psig)	Mean Drop Size (μm)	Air Temperature (°F)	Wind Speed (m/s)
6.6	1.6	10	23	315	92	3.3
13.4	3.4	12	43	287	90	3.1
28.1	6.4	16	56	326	87	3.4
56.4	12.6	20	92	318	90	3.3

[1] Gas denotes either HF or NH_3. The gas flow rate is approximately constant while the water flow rates vary. The gas plume enters the spray envelope with a uniform concentration of about 4 wt%.

[2] Bete TFNo.FCN, pointing downward.

Ammonia is less soluble in water than HF and, therefore, is removed to a lesser extent than HF by water spraying. Nevertheless, the predicted ammonia removal is sufficiently high (e.g., about 75 % at a 40 to 1 water to ammonia ratio) for water spraying to be an effective tool for mitigation of accidental release of ammonia as well.

It is emphasized that the assessment of the performance of a mitigation system requires modeling of the strongly-coupled mass transfer and momentum effects; calculations based only on mass transfer may result in erroneous results. Such an example is a paper presented at a recent meeting showing a water-curtain system, operating at water/NH_3 ratio of 1/1, as being capable of removing 60% to 70% of an ammonia release. The authors attributed their prediction to a proprietary mass transfer based computer program which they developed. Their conclusion was probably reached, because the mass transfer limitations caused by the drop residence times, the penetration of the plume through the spray envelope, and the dispersion of the small water droplets by the wind, were not taken into account. In fact, this system may be completely ineffective in removing ammonia vapor, because it sprays very little water and the sprays are very close to the release point. The water sprays are at the top of a vessel which is protected by a semi-closed dike. Small droplets sprayed in the upwind side of the ammonia tank, may reach the liquid ammonia pool in the dike and increase vaporization and subsequent risk to people downwind of the release. This example illustrates the complexity of phenomena related to spray mitigation, which can only be described by models of two-phase coupled mass, momentum and energy transfer.

3. EXTENSION OF HGSPRAY TO LNG RELEASES

The dispersal of Liquefied Natural Gas (LNG) vapor clouds with water spray curtains has been extensively investigated in wind tunnel and small-scale spill tests (Heskestad, 1983). These studies showed that well designed spray curtains can reduce LNG concentrations to under 5%. HGSPRAY is being expanded to model LNG dispersion, so that it can assist the design of either water spray or water cannon systems for this purpose. The enhancements to the model are associated primarily with heat transfer caused by the low temperatures in the LNG cloud. The heat released into the LNG vapor from the formation of ice in the water spray droplets is accounted for; then the loss of water due to icing and the thermal buoyancy of the cloud due to spray heating, are described. Also the absorption and ionization algorithms are decoupled. Verification of the new algorithms is in progress.

4. LINK OF FLUID MODELING WITH MATHEMATICAL MODELING

Fluid modeling of water sprays interacting with HF releases at an actual industrial facility, was conducted at Cermak Peterka and Petersen's (CPP) fluid modeling laboratory for Amoco Oil and for AlliedSignal. The purpose of these experiments was to develop site-specific data on near-field dispersion of an accidental release of HF. In these tests, hypothetical releases of HF at a 1/50 scaled down industrial site (with and without water sprays operating), were modeled using releases of ethane and SF_6 as a simulant gas (Blewitt et al, 1987; Petersen et al, 1993). A simulant gas was used because is not possible to scale simultaneously the atmospheric boundary layer, and the physics and chemistry of HF removal. The technique used in describing HF behavior in the wind tunnel, required matching HF concentrations, cloud density and plume velocity of actual, full-scale conditions to equivalent conditions in the wind tunnel. Fluid modeling provides a three-dimensional representation of the interaction of a plume with structures and water sprays. In addition it provides an estimate of dilution resulting from air entrainement by water sprays. It does not, however, describe removal of a water-soluble gas or vapor (e.g. HF, NH_3) by absorption in water drops. The physics and chemistry of such mass transfer and heat transfer between the vapor and water phases, are described by the mathematical model HGSPRAY. Fluid modeling provides important information on the crosswind characteristics of the vapor cloud as it intersects with sprays, which can not be obtained by the two-dimensional HGSPRAY. In general, if the released plume is not altered by structures on the site, data on the physical characteristics of a cloud (e.g, diameter, velocity, density, temperature, concentration) obtained by the HFPLUME component of HGSYSTEM, can be directly introduced into HGSPRAY as initial boundary conditions without the need for fluid modeling data (Figure 2). In the current study, however, several structures around the point of release influence the plume's shape and height and therefore, fluid modeling was required. The fluid modeling tests generated the initial concentration, velocity and turbulence profiles which were used as input to the HGSPRAY simulations.

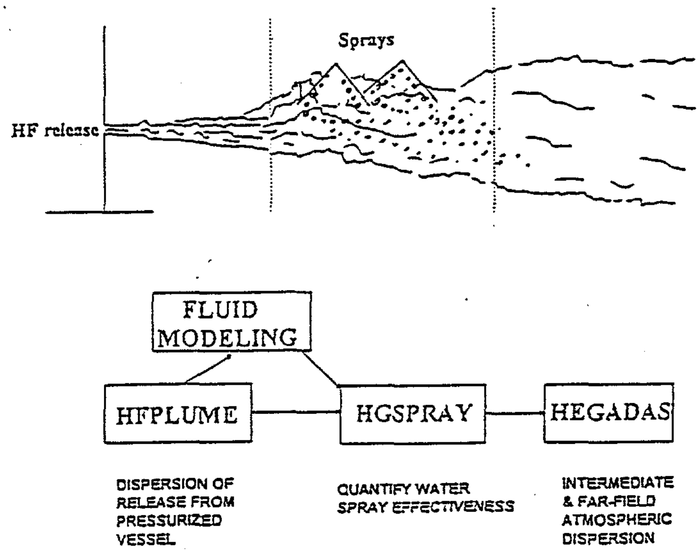

Figure 2. Mitigation Modeling Regimes

5. INTERFACE BETWEEN HGSPRAY AND HGSYSTEM

When evaluating the benefits of mitigation systems, it is important to evaluate such systems in terms of reduction of the downwind hazard zone. Thus while the percent removal is an important indicator of water spray performance, it is more important to examine how the mitigation system would reduce downwind exposure in the event of an accidental release. Impacts such as changes in cloud density and concentration due to the interaction of the vapor cloud and water spray can have a pronounced effect in the downwind exposure zone. This impies that dispersion modeling must be conducted after mitigation modeling, to estimate the downwind ambient air concentrations.

The HGSPRAY and HGSYSTEM models have been designed so that estimates on the properties of the cloud downwind of the water sprays are passed to the HEGADAS model. HEGADAS has the ability to start dispersion calculations at any point downwind using cloud property data. This approach (i.e., starting the dispersion calculations downwind of the water sprays) is more accurate than, for example, reducing the source term by the mitigation effectiveness and starting dispersion calculations from the point of release. The first approach takes into account the dilution of the cloud due to air entrainment and local structures, while the second does not.

6. MODELING RELEASES BETWEEN MONITORS

In the current application a release is sprayed by several monitors positioned both upstream and downstream of a release in different angles, settings and distances. To simulate such monitor configurations, a new version of the HGSPRAY model, HGSPRAY5b, was developed; the later, is capable of modeling a release of HF anywhere between fire water monitors. A release can be introduced within the computational space either as a point release of a specified flow rate, or as a line release of a specified concentration profile. HGSPRAY5 is also capable of modeling different types and different settings of fire water monitors and sprays in the same simulation allowing, therefore, discrimination between wide and narrow nozzle settings, different drop sizes, and angles of spraying.

7. CASE STUDIES

Two cases are considered, one involving sprays in a "curtain" setting and the other involving water monitors.

Case A -Water Curtain

This case involves modeling of an actual HF mitigation system based on sprays encircling an alkylation unit (Fthenakis and Blewitt, 1993). In the following we highlight elements of this study which illustrate the link between fluid and mathematical modeling.

1. Eight scenarios of release were identified after reviewing system, site and meteorological characteristics.
2. Fluid modeling experiments were conducted to generate concentration, velocity and turbulence data.
3. The air entrainment relationships of HGSPRAY were compared with the data obtained from the fluid modeling tests.
4. Simulations using HGSPRAY, produced estimates of the mitigation effectiveness of the system.

The spray configurations considered are: a) two headers at about 30 ft off the ground, one equipped with spray nozzles pointing upwards and the other with the same nozzles pointing downwards, and b) two headers at different elevations (e.g. 30 ft & 60 ft) with nozzles pointing horizontally toward the release. Two different types of spray nozzles producing drops of different size were tested. HF releases at two elevations and flow rates were considered to bracket the range of potential releases.

At grade (i.e., 1 m above the ground) the release rate was 43 kg/s and at a 15 m elevation the release flow rate was 37 kg/s. The water flow rate in the entire water curtain system was 33,000 gpm. The lateral spread and the concentration of the plume as it intersects the spray were determined from fluid modeling tests. According to the HGSPRAY simulations, the two-tier horizontal configuration removed HF somewhat more effectively than the up-and-down configuration for the specific release heights. Effectiveness of HF removal ranged from 70% for high wind speeds (e.g., 17 m/s) to 96% for light wind speeds (e.g., 5 m/s). The corresponding effectiveness of the up-and-down system ranged from 53% to 97%. The main reason for the advantage of the horizontal sprays, is that these sprays reached higher and covered elevated releases, whereas in the up-and-down configuration, a part of the plume escaped at the top. This behavior is illustrated by the concentration and velocity fields generated bv HGSPRAY (Figures 3 to 6).

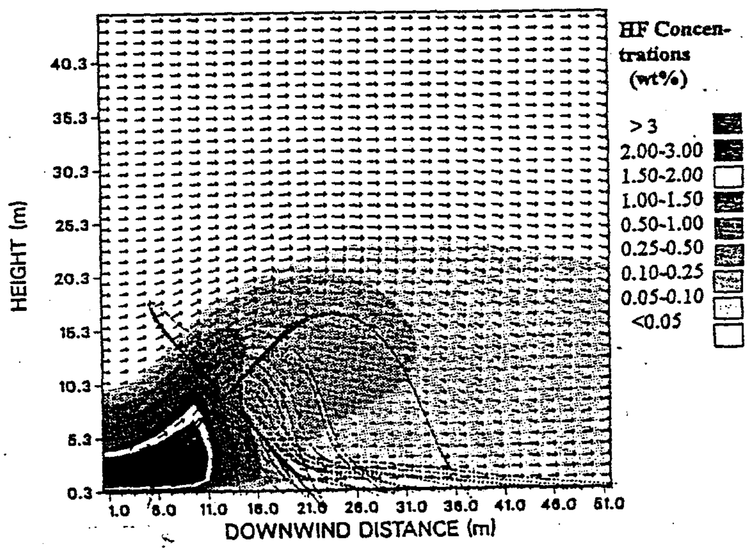

Figure 3. Up-and-Down Nozzles TF40FCN; u=5 m/s; Removal Effectiveness = 97%

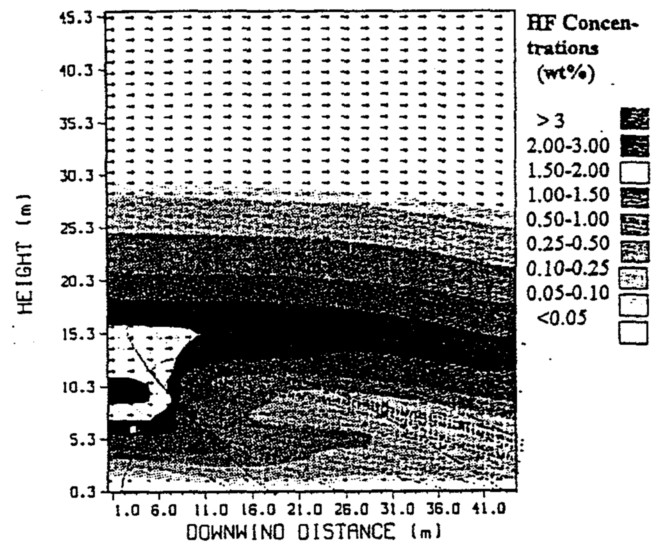

Figure 4. Up-and-Down Nozzles TF40FCN; u=17 m/s; Removal Effectiveness = 54%

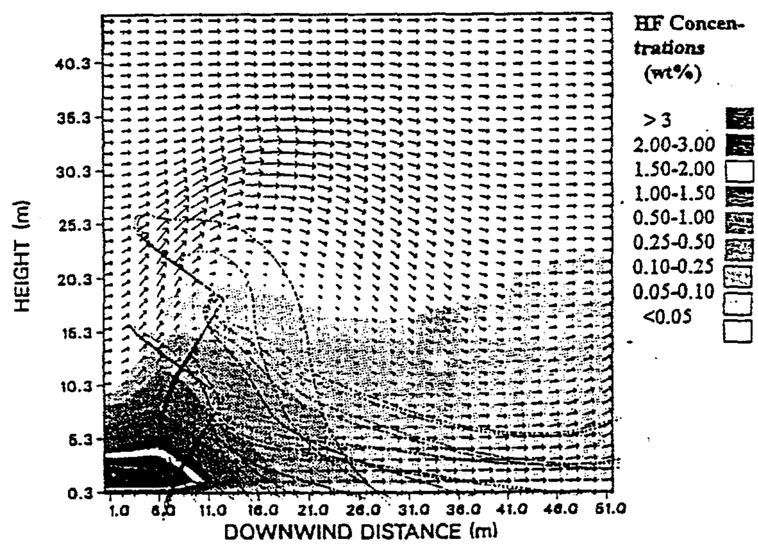

Figure 5. Inward Nozzles TF40FCN; u=5 m/s; Removal Effectiveness = 96%

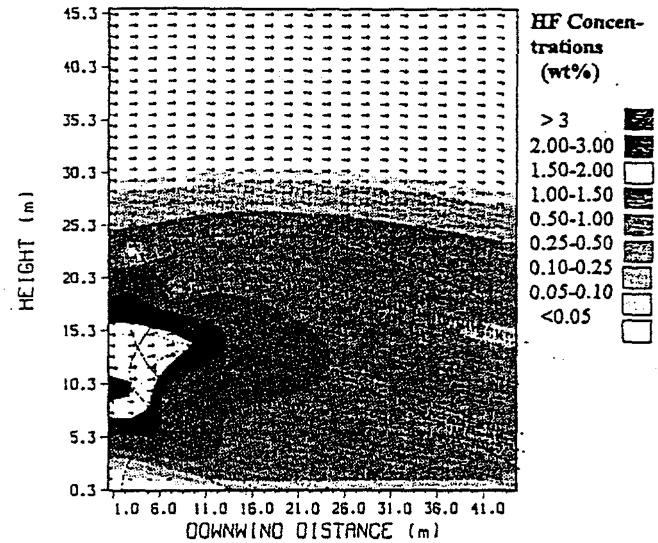

Figure 6. Inward Nozzles TF40FCN; u=17 m/s; Removal Effectiveness = 71%

In these figures, concentration fields are shown with different scales of gray, velocity fields by vectors showing velocity direction and magnitude, and the outer drop trajectories by darkened X- or V- like lines. Figures 3 and 4 show the predicted flow fields for the up-and-down configurations that bound the effectiveness range, and Figures 5 and 6 show the predicted flow fields of the horizontal configuration for the same scenarios of release.

Case B- Fire water-monitors

The model HGSPRAY5 has also been used to aid the design of mitigation systems comprising monitors placed around a potential release point. In this section we describe two sample simulations: i) a release of 3.4 kg/s of HF, under 3 m/s wind, sprayed by two monitors in wide setting; and ii) a 14 kg/s HF release under 10 m/s winds, sprayed by three monitors in narrow setting. Two-dimensional approximations of the monitor configuration were developed. For these cases we predicted removal <u>and</u> dilution effectiveness, defined as:

$$\text{Removal Effectiveness} = \frac{\text{Mass in - Mass out}}{\text{Mass in}}$$

where, Mass in and Mass out correspond to the HF mass flow rate upstream (inlet) and downstream (outlet) of the sprays;

$$\text{Concentration Reduction Effectiveness} = \frac{C_{in} - C_{out}}{C_{in}} = 1 - \frac{1}{DR}$$

where C_{in} and C_{out} are the average HF concentrations, upstream and downstream of the monitors, and DR is the Dilution Ratio defined as C_{in} / C_{out}. The average concentrations are calculated over the cross-section of the plume to a concentration of 30 ppm at the edges.

Figures 7 and 8 shows concentration contours, velocity vectors and water droplet trajectories for these simulations. In the first example, the removal effectiveness is a relatively low 60% due to the low initial concentration of the HF plume, but the dilution effectiveness is predicted to be about 92% (DR=12.5). In the second example, both removal and dilution effectiveness are high, 81% and 93% correspondingly. It is noted that the high water momentum produced by the monitors, makes spraying highly effective even at relatively strong wind conditions.

The reported dilution is due to spray action alone; the two-dimensional model doesn't describe the dilution of the plume in the cross-wind direction by gravity and friction with the ground and structures.

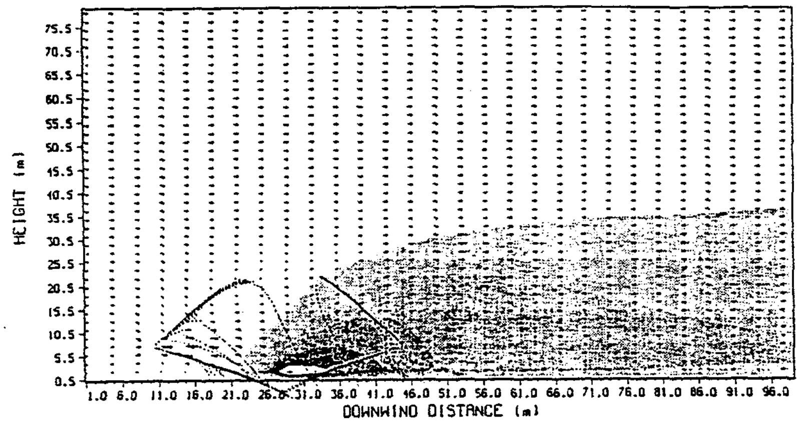

Figure 7. Monitors Upstream and Downstream of a Release; 5 gpm HF; u=3 m/s; Removal Effectiveness = 60%; Dilution Effectiveness = 92% (Dilution Ratio=12.5)

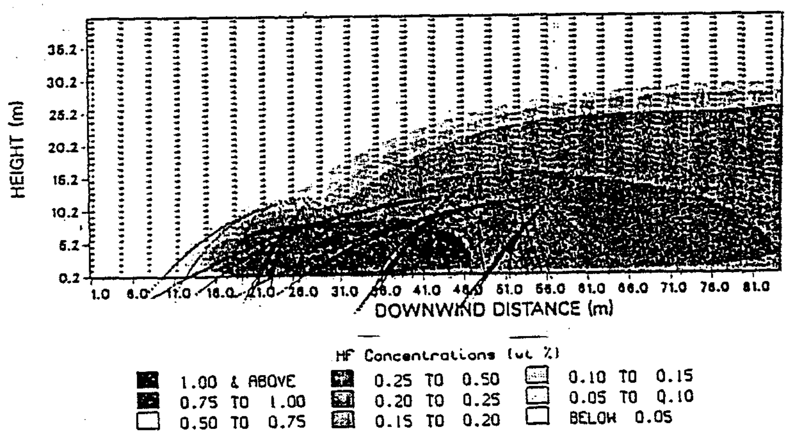

Figure 8. Monitors Downwind of a Release; 20 gpm HF; u=10 m/s; Removal Effectiveness = 81%; Dilution Effectiveness = 93% (Dilution Ratio=13)

Subsequent dilution is described by introducing the characteristics of the HF cloud downwind of the spray region, into the HEGADAS model. Thus, the downwind concentration reduction benefits of mitigation compared to an unmitigated release are estimated. Figure 9 shows an example of such modeling: maximum predicted concentration (60-minute average) as a function of downwind distance for three cases: 1) unmitigated release; 2) mitigated continuous release and 3) mitigated 10-minute release (assuming that the release was shut off after 10 minutes).

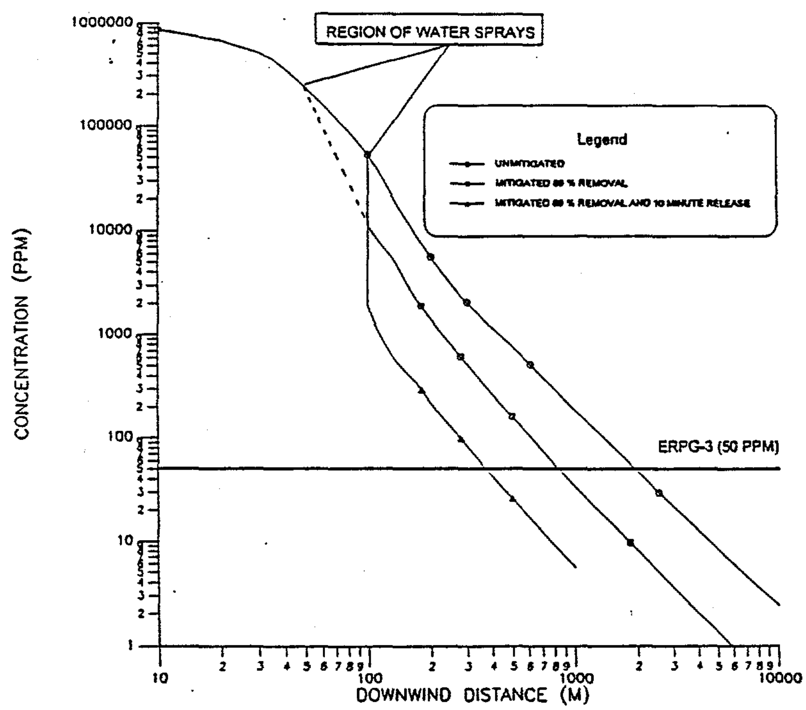

Figure 9. Predicted Downwind Concentration Reductions Caused by Water Spray Mitigation of a Hypothetical 14 kg/s HF Release.

The mitigation simulations were made using the breakpoint option in HEGADAS with the results from HGSPRAY5. The HEGADAS simulations were started at the end of the computational domain of HGSPRAY5 which was 100 m downwind from the point of releases. The 10-minute release duration was simulated using the finite release duration correction contained in HEGADASS. Also shown in Figure 9, is the ERPG-3[1] concentration level of 50 ppm. Without mitigation, the hazard zone to the ERPG-3 level extended to 2000 m downwind, whereas mitigation by water monitors reduced it to 800 m in the continuous release case and to 400 m in the 10-minute release case. In these simulations we assumed instantaneous detection and spray activation. The response time was not taken into account because the ERPG-3 level corresponds to 60-minute average concentration, a time interval significantly longer than anticipated detection and response times.

8. CONCLUSIONS

Modeling of the interactions of water sprays or fire water monitors with an unconfined gaseous release, can assist the design of water-based mitigation systems. A new version of the computer code HGSPRAY (HGSPRAY5), is capable of modeling several sprays or fire water monitors in upstream and downstream positions. It simulates a gaseous release anywhere between sprays or monitors, allows for different types/settings of nozzles to be modeled in the same simulation, and allows for specification of different velocity and turbulence profiles. Nevertheless, the application of this model to describing the flow fields

[1] ERPG-3 is 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 life threatening health effects.

induced by fire water monitors spraying from various positions, requires considerable simplification of complex three-dimensional fields, and poses significant constraints in its application. Releases in the downwind direction sprayed uniformly by water sprays encircling the point of release, generate in many cases flow fields that can be simulated using the model HGSPRAY with the initial plume conditions predicted by HGPLUME. The effect of the structures on the dispersion of a plume released in an actual facility can not, however, be described by these models. In cases, therefore, of a dense facility, fluid modeling is necessary to determine the plume characteristics in the lateral direction and provide accurate input into HGSPRAY.

The HGSPRAY5b model is capable of predicting the performance of water-spray systems in mitigating water-soluble gases (e.g., HF and NH_3), via absorption and dilution, and in reducing the concentration of flammable vapors (e.g., LNG), via dilution. These predictions require accurate modeling of strongly-coupled mass transfer and momentum effects, and of heat transfer effects as well. Attempts to model such systems based only on mass transfer considerations, may result in erroneous results.

9. REFERENCES

Blewitt, D.N.,Yohn J.F., Koopman R.P., Brown T.C., and Hague W.J., Effectiveness of water sprays on mitigating anhydrous hydrofluoric acid releases, Proceedings of the International Conference on Vapor Cloud Modeling, pp. 155-171, Nov 2-4, 1987, published by the American Institute of Chemical Engineers, (ed. J. Woodward).

Dasgupta P.K. and Dong S., Solubility of Ammonia in Liquid Water and Generation of Trace Levels of

Standard Gaseous Ammonia, Atmospheric Environment, 20(3), 565-570, 1986.

Fthenakis, V.M., The feasibility of controlling unconfined releases of toxic gases by liquid spraying, *Chemical Engineering Communications*, 83, 173-189 ,1989.

Fthenakis, V.M. and Zakkay V., A Theoretical Study of Absorption of Toxic Gases by Spraying, *Journal of Loss Prevention*, 3, 197-206, 1990.

Fthenakis, V.M., Schatz, K.W. and Zakkay V., Modeling of Water Spraying of Field Releases of Hydrogen Fluoride, Proceedings of the International Conference and Workshop on Modeling & Mitigating the Consequences of Hazardous Materials, New Orleans, May 20-25, 1991, AIChE, NY, pp. 403-427

Fthenakis V.M. and Blewitt N.D., Mitigation of HF Releases: Simulation of the Performance of Water Spraying Systems, J. Loss Prevention, 6(4), 209-218, 1993

Heskestad G., Dispersal of LNG Vapor Clouds with Water Spray Curtains, Final Report, GR1-83/0019, Gas Research Institute, 1983.

Petersen R. L., and Blewitt D.N., Evaluation of Water Spray/Fire Monitor Mitigation Systems for Two Refineries, Proceedings of 1992 ProcessPlant Safety Symposium, AIChE, Vol. 1., pp. 477-486, 1992

Petersen R. L.,, Parce D.K., and Ratcliff M.A., Wind Tunnel Modeling of Water Spray Mitigation Systems, Report Prepared by Cermak Perka Petersen, Inc. For AlliedSignal Inc., June 1993.

Puttock J.S. et. al, Development and Validation of Atmospheric Dispersion Models for Hydrogen Fluoride, Shell Research Limited, Chester, England, Technical Report, 1990.

Schatz K.W. and Koopman R.P., Effectiveness of Water Spray Mitigation Systems for Accidental Releases of Hydrogen Fluoride; Industry Cooperative HF Mitigation / Assessment Program, final draft, Volume I, June 1989 and Volume VIII, May 1992.