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A PROPELLANT AND CHEMICAL SPILL AND DISPERSION MODEL

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1.0 ABSTRACT

Many of the chemicals, propellants and oxidizers handled and used by the defense agencies and NASA produce heavier-than-air vapors if released into the atmosphere. Some of the chemicals, such as nitrogen tetroxide, may react with ambient moisture resulting in the formation of nitric acid vapors and liquid aerosols. Other chemicals, such as liquefied gases, when released flash vaporize and form vapor clouds containing airborne liquid aerosols. All of these vapor clouds have mean densities higher than that of ambient air and consequently disperse in the atmosphere in a manner completely different from the dispersion and dilution of a neutral density cloud.

A dense gas dispersion model has been developed (called "Air Force Dispersion Assessment Model" - ADAM) which takes into consideration a variety of release types (instantaneous; continuous; puff and jet releases; liquid, gas or two-phase; diked tanks, undiked tanks; fixed facilities, transports, etc.). The model includes the effects of liquid aerosols on the cloud or plume behavior, reaction kinetics of the chemical-water vapor mixing and the entrainment of air. Atmospheric stability is represented on a continuous scale from the extremely unstable to extremely stable. The dispersion model is a hybrid box-volume source Gaussian model.

The ADAM dispersion model is applicable to most chemicals of interest. The model, at present, includes the thermodynamic modules for nitrogen tetroxide, ammonia, chlorine, phosgene, hydrogen sulphide and sulphur dioxide. The dispersion of any other reactive chemical can easily be evaluated by adding only the thermodynamic module relevant to the chemical.

The results from the model have been compared to test data from field experiments conducted over the past 40 years involving the release of several chemicals of interest to the defense services.

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<p>The defense services transport, store and use many kinds of chemicals including fuels, oxidizers, propellants and weapons related chemicals. Many of these chemicals are volatile and may form dense vapor clouds if they are released into the atmosphere. Depending on the physical properties of the chemical, storage conditions, release conditions and weather conditions different types of vapor clouds may be formed (heavy clouds, aerosol bearing clouds, instantaneous puffs, continuous plumes, etc.). In addition, some of the chemicals may react with ambient moisture. It has been shown in the literature that the behavior of heavy vapor clouds is considerably different from that of neutral density vapor clouds.</p>			
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We have developed a model that takes into consideration the determination of vapor source strengths from over 18 different release scenarios. The model includes puff releases, jet releases and plume releases, with or without aerosols. The dispersion of the heavy vapor cloud or plume resulting from the source is modeled. The thermodynamics and kinetics of the reaction of the chemical with the ambient moisture has been modeled for several common chemicals (N₂O₄, Ammonia, Phosgene, Chlorine, etc.) of interest to the defense services. These thermodynamic models have been incorporated into the dispersion models. Heavy gas dispersion of the chemical vapors, evaporation of the aerosols, and other related phenomena have been modeled. The model also smoothly transits to a passive, Gaussian dispersion phase when the density difference between the dispersing cloud and the atmospheric air is small.

The results from the model developed have been compared to test data from field experiments conducted over the past 40 years involving the release of several chemicals of interest to the defense services. These chemicals include, phosgene, chlorine, anhydrous ammonia, nitrogen tetroxide and freon. These test have been conducted over different weather conditions, terrains (including over the sea) and release conditions (instantaneous releases, explosive releases, and continuous releases of pressurized liquids). The quantities released range from small volumes to very large vapor volumes (2000 m³). We have compared our model results with the data from these field tests. The results compared include: (i) the variation of peak concentration at ground level as a function of distance, (ii) the spread area of the vapor cloud at different down wind locations, (iii) the acceleration and down wind velocity of a puff of vapor, (iv) the jet length, depth and horizontal cross wind extent in the case of continuous releases and (v) the far field concentration corridors. The agreement between the field test data and the model results is extremely good.

The entire source and the dispersion models, including the effects of reaction, runs on an IBM-AT type personal computer with execution times on the order of 2 minutes. The toxic corridors and other results can be displayed graphically to scale on the monitor or superimposed on a digitized map of the area of interest.

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The ADAM model runs on an IBM-AT type personal computer with execution times on the order of 2 minutes. The toxic corridors and other results can be displayed graphically to scale on the monitor or superimposed on a digitized map of the area of interest.

2.0 DESCRIPTION OF HEAVY VAPOR CLOUD DILUTION

When a vapor cloud* which is heavier than air due to its vapor density or the combined density of vapor and any aerosols is released** into the atmosphere, it undergoes dilution in different stages. Depending on the nature of release (explosive, passive, jet, etc.), there may be an initial rapid entrainment of air into the cloud. The cloud next goes through a gravitational slumping stage due to its excess density. During this second stage, the lateral dimensions of the cloud increase due to gravity driven flows and the cloud is accelerated downwind due to momentum transfer from the wind. The entrainment of air is primarily controlled by the density stratification in the cloud and by the lateral spread rate. When the cloud density is within a few percent of the density of air, a third stage of dispersion occurs in which the dilution of the cloud depends on both the atmospheric turbulence characteristics as well as the cloud density. In the fourth and final stage, the cloud dilution is due principally to atmospheric turbulence.

Air is entrained into the cloud primarily at the edges and at the top. Therefore, the concentration of the chemical decreases first at the edges and the top. The chemical

* The term "vapor cloud" used in this paper is assumed to mean both a puff of vapor and a plume.

** We have modeled a variety of chemical release modes and sources (pressurized liquid release, instantaneous & continuous, cryogenic liquid release, gas release, etc.). The details of these sources and models to determine source strength have been published in a recent report (Raj and Morris, 1987).

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concentration at the core remains high until sufficient air has diffused into the central regions. If there is chemical reaction, the concentrations of the products of reaction are high at the edges and the top. In effect, in a real cloud the concentrations within the cloud are non-uniform and may show distinct bi-modal distributions in the lateral direction for reaction products. However, as the dilution continues, it is anticipated that the reaction product distributions will show a more uniform or modified Gaussian type distributions.

Our approach in modeling the above phenomena is based on the assumption that the chemical reaction, if any, and the dispersion process can be decoupled. The interaction between the two processes occurs through the overall density of the cloud. That is, the air entrainment rate is determined by the overall density of the cloud and the meteorological conditions. The overall density of the cloud and the mean concentration of the species in the cloud at any instant of time are determined solely by: (i) the mass, phase, and thermodynamic conditions of the chemical at release, (ii) the mass of air mixed, its temperature and humidity, and (iii) the total net heat input into the cloud from external sources. Our second assumption is that reaction between air and the chemical ceases when the concentration of the primary chemical is very low. In fact, we assume that no reaction occurs after the transition from the heavy gas dominated dispersion to the atmospheric dominated dispersion. The third assumption in our model is that the initial stages of dispersion can be described by a modified "box" model and the atmospheric dispersion stage is described using a modified Gaussian, volume source based model. The details of these are described in the appropriate sections below.

3.0 CHEMICAL EFFECTS

Many different types of behavior are possible if a chemical vapor is released into the atmosphere and it contains liquid aerosols (which may react with water vapor or air). The first type is the one in which the cloud formed is heavier than air and contains liquid aerosols. The chemical may not react with the air or water vapor and liquid aerosols may not dissolve in liquid water (ex., chlorine). In this case, the entrainment of air into the cloud lowers the vapor concentration and the chemical vapor pressure. The aerosols evaporate at the expense of the sensible heat of the cloud and, in the absence of any external heating, depress the cloud temperature. The density of the cloud increases due to the lowering of temperature.

A second type of chemicals normally behave as above, but have a completely different behavior when liquid water drops are present in the cloud (due to rain, fog, snow or water droplets from a fireman's hose). A classic example of this is phosgene. If no liquid water is present in the cloud, phosgene vapor and aerosols are not reactive with water vapor in the atmosphere. If liquid water drops are present due to condensation or other

reasons, however, phosgene liquid aerosols readily dissolve in water forming hydrochloric acid drops and carbon dioxide vapor. These types of behaviors obviously have profound influences on dispersion predictions.

The third type of chemical behavior is exemplified by the release of a high vapor pressure liquid into the atmosphere (ex., anhydrous ammonia). In this case, the cold vapor-aerosol cloud formed after release condenses moisture from the atmosphere. The anhydrous aerosols dissolve in the condensed water forming aqueous liquid aerosols. These liquid droplets can persist for a long time if the partial vapor pressure of the chemical over a dilute aqueous mixture is very low.

The fourth type of behavior involves spontaneous dissociation and/or reaction of a chemical with the moisture in the atmosphere, producing new chemical species. These new species may condense, depending on their partial pressure, and form liquid chemical aerosols. These formations have profound effects on the vapor cloud temperature, density and on the cloud size. Hazards may be posed by the secondary product chemicals as well as by the primary chemical. The aerosols formed may be very stable and persist for a considerable distance. In addition, the aerosols may extend the region over which the cloud behaves as a heavy gas. Example chemicals for this type of behavior are nitrogen tetroxide (N_2O_4) and hydrogen fluoride (HF). N_2O_4 forms nitrogen dioxide by dissociation and forms nitric acid aerosols due to reaction with the moisture in the atmosphere. The nitric acid further dissolves in the water and forms aqueous nitric acid aerosols which may persist until considerable dilution of the cloud has occurred.

The overall model calculation procedure is illustrated in the flow diagram shown in Figure 1. The user inputs a variety of data through easy-to-use menus. (Selected data from a default file can be overridden by the user.) There are four subsystem modules containing (i) source models, (ii) models to represent atmospheric parameters, (iii) thermodynamic models, and (iv) dispersion models. In addition, a chemical property database (library) is also a part of the system. The output is graphically displayed as concentration or dose isopleths. In addition, the output results are stored in numeric files.

4.0 DISPERSION MODEL

The principal feature of our dispersion model is that it simulates the density dominated dispersion phase as well as the dispersion in the passive (near neutral density) regime without having to resort to equivalent point sources, invoking transition criteria, etc. The dispersion of both heavy plumes as well as puffs are modeled. The initial conditions of the vapor puff (or plume) are calculated using the source models and the thermodynamic models. The starting condition for a puff is a

cylindrical box and for a plume is a given flow rate through a rectangular "window" of specified dimensions. In both cases, the thermodynamic condition of the vapor air mixture is fully specified.

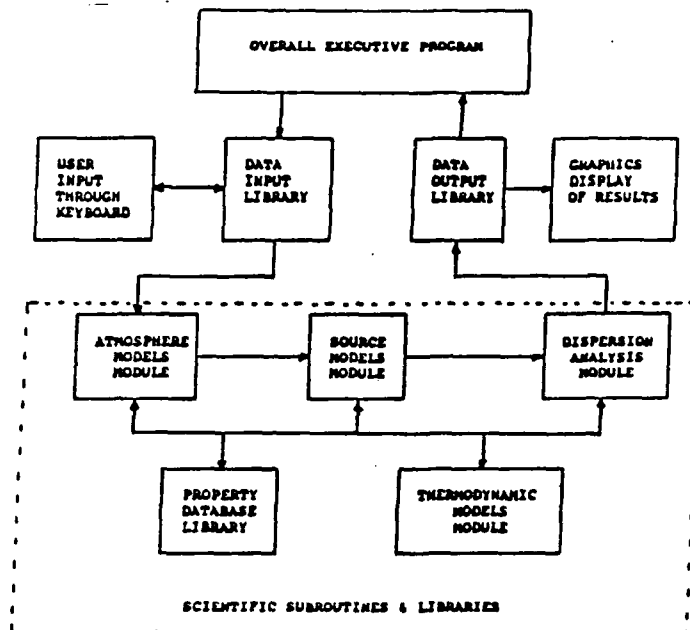


Figure 1: Dispersion Model Submodules and Calculation Flow Chart

The details of the dispersion model are illustrated schematically in Figure 2 and Figure 3 for the case of a puff dispersion (a similar approach is used for plumes also). The cylindrical cloud at position A (at $X = 0$) is subject to a wind speed U_{10} . Air is entrained at the top and on the sides. Also the cylindrical cloud expands radially due to gravitational collapse. The cloud is also accelerated by the prevailing wind. In our model, it is assumed that the vapor concentration distribution is radially symmetric.

Referring to Figure 3, the initial concentration and other intensive properties (temperature, aerosol fractions, etc.) are uniform ("Top Hat") within the initial cylindrical box (at $X = 0$). As the cloud moves downwind and entrains air, the top hat concentration profile is smoothed at the edges by side (and top) entrainment with the central core still having a uniform, but lower, concentration. If all of the core is diluted, the concentration distribution in the puff is essentially Gaussian.

The above physical process is simulated in our model by the following process. We recognize that the dilution and puff expansion is due to two simultaneous processes. The first one is due to gravitational expansion and air entrainment associated with it. The second is due to the effect of ambient turbulence. We treat these effects as being linearly superposed. First, we

model the gravitationally driven radial expansion, downwind motion and air entrainment using the classic "box" approach (for detailed mathematical representations, we refer the reader to several literature citations such as, Havens, 1982; Jagger, 1983; Raj, 1986; Raj, 1985; Weber, 1983). The air entrained into the box is assumed to react with the chemical and result in a downwind cylindrical box at location X with uniform concentration C_x and other properties which are also top hat distributed. This is shown in Figure 3.

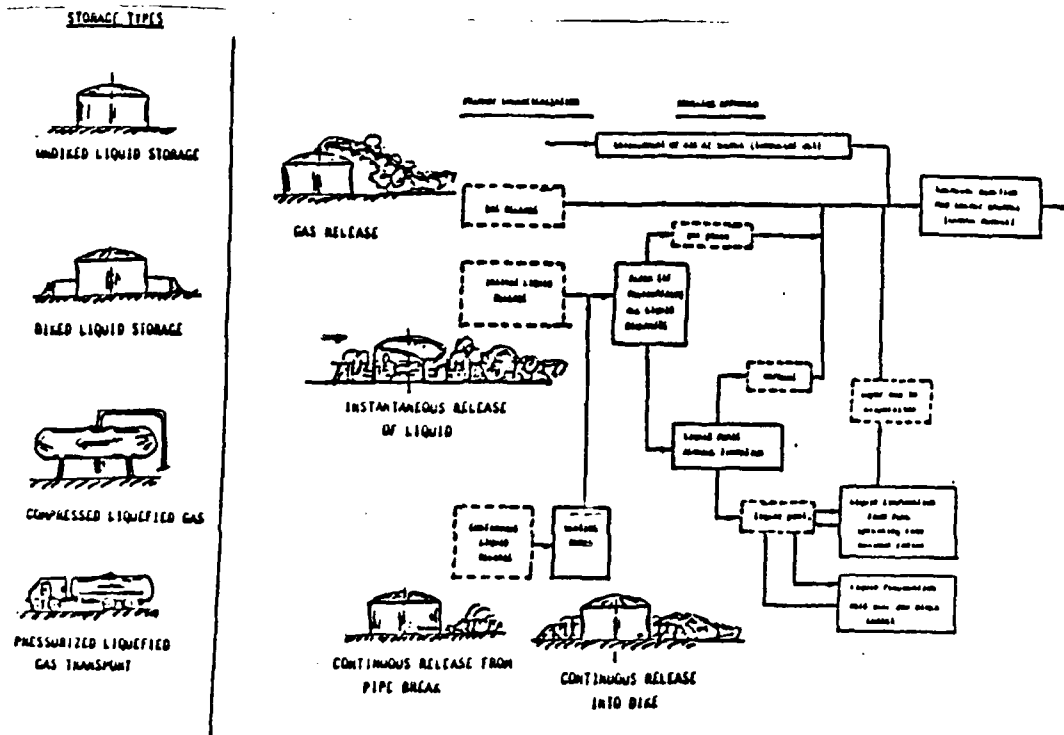


Figure 2: Different Types of Releases Modeled

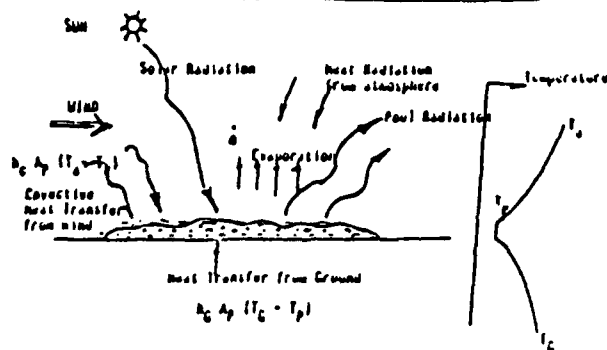


Figure 3: Schematic Representation of Heat Transfer to a Liquid Pool on the Ground

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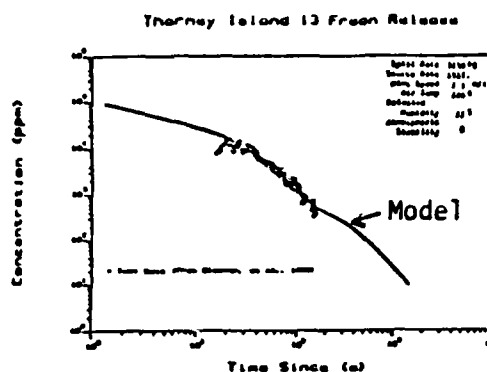


Figure 10: Comparison of Model Predictions for Downwind Centerline Concentration with Test Data from Thorney Island 13 Freon Release

In all of the model runs, only the conditions of the releases and the chemicals were changed. The model internal parameters (constants in entrainment, friction and other equations) were kept the same in all comparisons. It is seen that in all cases the model predicts the concentration data exceedingly correctly. Also, the predictions are uniformly accurate both in the heavy gas regime () and in the passive dispersion regime (Figure 7) and in the transition regions. The model predicts reasonably accurately the observed cloud height, the area of spread as a function of time and the times of arrival of puffs at given distances.

The entire model described in this paper runs on an IBM-AT type computer and calculation times range from 30 seconds to 1.5 minutes. The results are plotted on a graphics screen.

This model was developed under a U.S. Air Force project and is intended to be used for determining toxic corridors arising from the release of chemicals which form heavy gas clouds or plumes. This model will be an adjunct to the AFTOX model currently being used by the U.S. Air Force. The model is useful for determining the toxic corridors arising from the release of chemicals from both: (i) transportation, launch pad area and storage tank accidents, and 2) chemical weapons.

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topographic conditions. The comparisons have included downwind ground level concentration variation as a function of distance, height and width of visible clouds and plumes, cloud temperatures, and cloud arrival times. Details of the comparisons are given in our report (Raj & Morris, 1987). Only a sample of these comparisons are presented here.

Figure 6 shows predicted and measured concentrations for the explosive release of phosgene. The cloud contained a significant quantity of liquid aerosols. Figure 7 shows similar results for a continuous release of chlorine on the ocean. The results for a continuous release of anhydrous ammonia are shown in Figure 8. Figure 9 shows the results for nitrogen tetroxide and shows results from one of the tests of the Thorney Island Series involving the instantaneous release of freon.

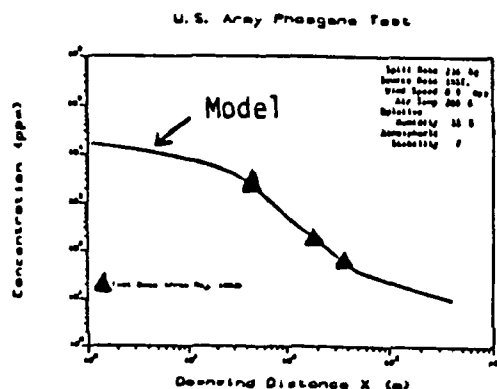


Figure 6: Comparison of Model Predictions for Downwind Centerline Concentration with Test Data from U.S. Army Phosgene Test

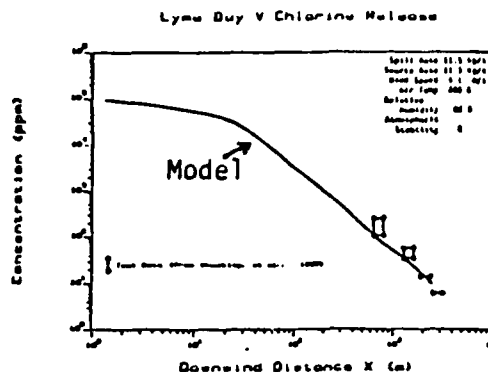


Figure 7: Comparison of Model Predictions for Downwind Centerline Concentration with Test Data from Lyme Bay V Chlorine Release

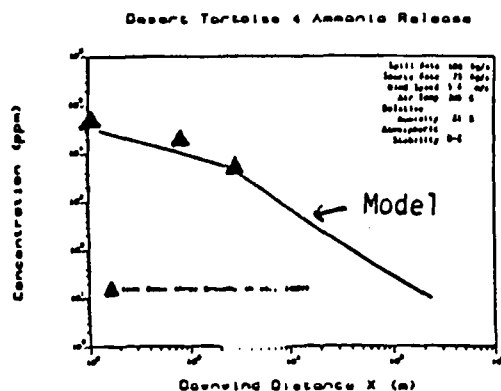


Figure 8: Comparison of Model Predictions for Downwind Centerline Concentration with Test Data from Desert Tortoise 4 Ammonia Release

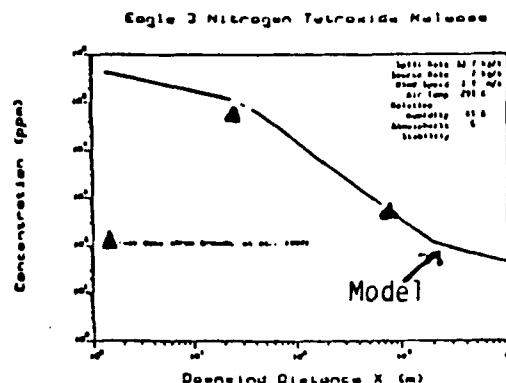


Figure 9: Comparison of Model Predictions for Downwind Centerline Concentration with Test Data from Eagle 3 Nitrogen Tetroxide Release

The modeling can be very simple if the chemical is not reactive. The analysis can become very complex if the chemical reacts with water or air leading to the formation of new species which may be distributed in vapor and condensed phase (as in the case of nitrogen tetroxide reaction with water vapor). Details of the chemical reaction models for 6 chemicals (including N_2O_4) are indicated in our report (Raj & Morris, 1987). An example of the calculation of the final state of the mixture for the mixing of N_2O_4 vapor and humid air was described in detail in our earlier paper (Raj, et al., 1987).

Typical results from this model for N_2O_4 -Humid Air mixing are indicated in Figure 4 and Figure 5. The variation of N_2O_4 -Vapor Air mixture temperature as a function of dilution is shown in Figure 4. The initial decrease in temperature is due to the dissociation of N_2O_4 to NO_2 . Figure 5 shows the concentration of water vapor in an equilibrium mixture of N_2O_4 vapor and humid air of different relative humidities at different dilutions. Also plotted on the same figure is the saturated water vapor concentration in air of different humidities at mixture temperature (dotted line). It is clear that in the region where saturated water vapor concentration is lower than that calculated by gas mixture model (solid lines) condensation of water in the form of fog will occur. This will lead to the dissolution of nitric acid vapors forming aqueous nitric acid fog (or aerosols). The results clearly show how even when the original chemical does not have any aerosols, spontaneous condensation and formation of a new reaction product species can occur.

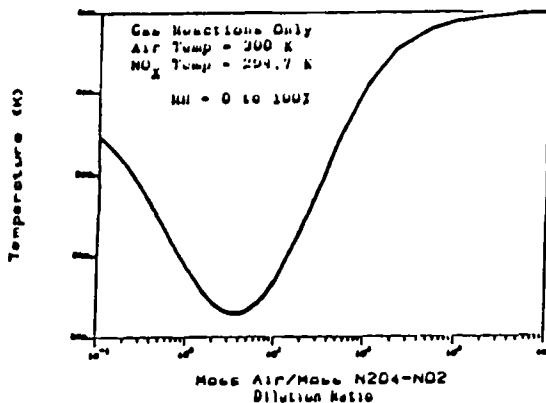


Figure 4: Reaction Temperature of N_2O_4 -Humid Air System

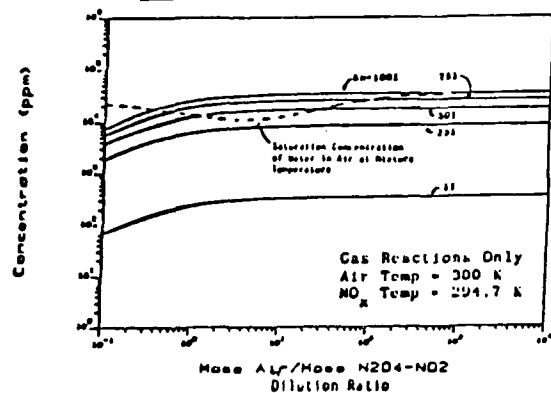


Figure 5: Concentration of Water in Equilibrium Mixtures of N_2O_4 - NO_2 and Humid Air for Various Air Humidities

7.0 COMPARISON OF DISPERSION MODEL RESULTS WITH FIELD TEST DATA

We have compared the results from the model with most of the available field test data for a variety of chemicals (some reactive), different release types and atmospheric and

To obtain the real concentration distribution at X , we now assume that the box at X with its C_x concentration and dimension R_x and H_x is dispersing from $X = 0$ to $X = X$ under the influence of atmospheric turbulence only. To describe the latter dilution, we use the volume source Gaussian model (Raj & Morris, 1987) on a source of dimensions R_x , H_x , and uniform concentration C_x located at $X = 0$. This model then gives the distribution of concentration in a puff whose center is located at X and which has the characteristics of "wings" on the sides and uniform core in the center.

The above procedure can be continued until the center line ground level concentration is equal to the specified concentration. Also at every X , the width of a contour of specified concentration can be determined. To conserve computational time, we use only the volume source Gaussian model to describe the dispersion in the far field; i.e., when the local Richardson number is less than 1. The standard deviation values used in the atmospheric turbulence induced dilutions are the Pasquill-Gifford values (Slade, 1968) modified to take into account the effects of aerodynamic roughness and the concentration averaging time.

Model equations have been presented in an earlier paper (Raj, et al., 1987). More complete details including assumptions and equation simplifications are described in our recent report (Raj and Morris). Therefore, model description in terms of equations is not presented here.

5.0 ATMOSPHERIC STABILITY

We calculate the atmospheric stability using the methodology suggested by Kunkel (1985). This method is based on Golder's method (1972), but classifies the atmospheric stability on a continuous scale from extremely stable to extremely unstable. The standard deviation values are corrected for roughness and averaging times. The method utilizes either the measured wind angle standard deviations (and time of day) or the solar heat input, time of day, wind speed data, surface roughness, etc. to calculate the atmospheric stability.

6.0 CHEMICAL REACTION CONSIDERATIONS

The mixing of the chemical and ambient air is modeled using equilibrium thermodynamic approach. A unit mass of the chemical at an initial specified state is mixed isobarically with "m" units of humid air from the atmosphere. There is a heat exchange of Q units of energy within the universe. The final mixture thermodynamic conditions are determined by applying the equation of mass and energy conservation together with phase equilibria relationship and reaction kinetics. The final mixture state is expressed by its temperature, density, number of species in vapor phase, the number in liquid phase, vapor and liquid phase specie concentrations.